

BULLETIN  
DE  
L'ACADÉMIE POLONAISE  
DES SCIENCES

Rédacteur en chef  
K. KURATOWSKI

Rédacteur en chef suppléant  
S. KULCZYŃSKI

CLASSE TROISIÈME

Rédacteur de la Série  
L. INFELD

Comité de Rédaction de la Série  
K. BORSUK, S. LESZCZYCKI, J. SAMSONOWICZ, M. ŚMIAŁOWSKI

VOLUME II  
NUMÉRO 2

VARSOVIE 1954

PRINTED IN POLAND

PAŃSTWOWE WYDAWNICTWO NAUKOWE — WARSZAWA 1954

<i>Nakład 1019 + 100 egz.</i>	<i>Rękopis dostarczono 19. XII. 1953</i>
<i>Ark. wyd. 3.5, ark. druk. 3<math>\frac{1}{4}</math></i>	<i>Podpisano do druku 18. III. 1954</i>
<i>Papier bezdrzewny sat. 80 g, kl. III</i>	<i>Druk ukończono 31. III. 1954</i>
<i>Format B 5, 70×100 cm</i>	<i>Zam. prod. 58/54    Cena zł 5,—</i>

KRAKOWSKA Drukarnia Naukowa, KRAKÓW, UL. CZAPSKICH 4

# Sur une proposition équivalente à l'existence d'un ensemble de nombres réels de puissance $\aleph_1$

par

W. SIERPIŃSKI

*Présenté à la séance du 14 Décembre 1953*

A. Mostowski a posé récemment la question suivante: quelles sont les conséquences de l'hypothèse de l'existence d'une fonction qui fait correspondre à tout ensemble dénombrable de nombres réels un nombre réel n'appartenant pas à cet ensemble?

Je démontrerai ici (sans faire appel à l'axiome du choix) le théorème suivant:

**Théorème.** *Les deux propositions suivantes  $P_1$  et  $P_2$  sont équivalentes:*

$P_1$  *Il existe une fonction  $f$  qui fait correspondre à tout ensemble dénombrable  $D$  de nombres réels un nombre réel  $f(D) \notin D$ .*

$P_2$  *Il existe un ensemble de nombres réels de puissance  $\aleph_1$ .*

**Démonstration.** I.  $P_1 \rightarrow P_2$ . Supposons que la proposition  $P_1$  est vraie et soit  $D_1 = \{1, 2, 3, \dots\}$ ,  $x_1 = f(D_1)$ . Soit  $\alpha$  un nombre ordinal donné tel que  $1 < \alpha < \Omega$  et supposons que nous avons défini tous les nombres réels  $x_\xi$  pour  $\xi < \alpha$ . Soit  $D_\alpha$  l'ensemble formé de tous les nombres naturels et de tous les nombres  $x_\xi$ , où  $\xi < \alpha$ ; l'ensemble  $D_\alpha$  est dénombrable puisque  $\alpha < \Omega$ ;  $x_\alpha = f(D_\alpha)$  est donc un nombre réel bien défini par la fonction  $f$ . Les nombres  $x_\alpha$  sont ainsi définis pour  $\alpha < \Omega$  par l'induction transfinie. Vu la définition des ensembles  $D_\alpha$  on a pour  $\alpha < \beta < \Omega$ ,  $x_\alpha \in D_\beta$  et comme, d'après la propriété de la fonction  $f$ ,  $x_\beta = f(D_\beta) \notin D_\beta$ , on a  $x_\alpha \neq x_\beta$  pour  $\alpha < \beta < \Omega$ : les termes de la suite transfinie  $\{x_\alpha\}_{\alpha < \Omega}$  sont donc tous distincts. L'ensemble  $A$  de tous les nombres  $x_\xi$ , où  $\xi < \Omega$ , a donc la même puissance que l'ensemble de tous les nombres ordinaux  $< \Omega$ , il donc est de puissance  $\aleph_1$ . La proposition  $P_1$  implique donc l'existence d'un ensemble de nombres réels de puissance  $\aleph_1$ , c'est-à-dire qu'elle implique la proposition  $P_2$ .

II.  $P_2 \rightarrow P_1$ . Supposons que la proposition  $P_2$  est vraie: il existe un ensemble de nombres réels  $A$  de puissance  $\aleph_1$ , donc de même puissance que l'ensemble de tous les nombres ordinaux  $< \Omega$ . Il existe par conséquent une suite transfinie  $\{x_\xi\}_{\xi < \Omega}$  formée de tous les nombres de l'ensemble  $A$ . Soit  $D$

un ensemble dénombrable quelconque de nombres réels. L'ensemble  $A$  étant indénombrable, on a  $A - D \neq 0$ . Il existe donc, dans la suite  $\{x_\xi\}_{\xi < \omega}$ , des termes qui n'appartiennent pas à  $D$ ; désignons par  $f(D)$  le premier parmi eux. La fonction  $f$  fait donc correspondre à tout ensemble dénombrable  $D$  de nombres réels un nombre réel n'appartenant pas à  $D$ . La proposition  $P_1$  est donc vraie.

L'équivalence des propositions  $P_1$  et  $P_2$  est ainsi démontrée.

Notre théorème se trouve ainsi démontré.

On voit sans peine quelles modifications demanderait notre démonstration pour que l'on puisse prouver l'équivalence des propositions  $P_1$  et  $P'_2$  suivantes:  $P'_1$ . Nous savons définir une fonction  $f$  qui fait correspondre à tout ensemble dénombrable  $D$  de nombres réels un nombre réel  $f(D) \in D$ .

$P'_2$ . Nous savons définir un ensemble ordonné de type  $\omega$  de nombres réels.

Ajoutons que d'après un théorème bien connu on sait définir une fonction qui fait correspondre à toute suite infinie de nombres réels un nombre réel distinct de tout terme de cette suite.

Institut de Mathématique de l'Académie Polonaise des Sciences



# The Problem of Uniqueness for the Solution of a System of Partial Differential Equations

by  
A. PLIŚ

*Communicated by T. WAŻEWSKI at the meeting of December 14, 1953*

Let us suppose that the coefficients  $a_{ij}(x, y)$  ( $i, j = 1, 2, \dots, m$ ) of the system of differential equations

$$(1) \quad \frac{\partial u_i}{\partial x} = \sum_{j=1}^m a_{ij}(x, y) \frac{\partial u_j}{\partial y} + b_{ij}(x, y) u_j \quad (i = 1, 2, 3, \dots, m)$$

are twice differentiable, the coefficients  $b_{ij}(x, y)$  are continuous and the characteristic values of the matrix  $\|a_{ij}(x, y)\|$  are distinct in a certain neighbourhood  $W$  of the point  $(0, 0)$ . T. Carleman [1] proved that under these assumptions every solution of class  $C^1$  in the neighbourhood  $W$ , satisfying system (1) in the neighbourhood  $W$  and the initial conditions:

$$u_i(0, y) = 0 \quad (i = 1, 2, \dots, m)$$

for  $|y|$  sufficiently small, vanishes identically in a certain neighbourhood of the point  $(0, 0)$ .

In this note we give an example of a system\*) of form (1) ( $m = 2$ ) which fulfils all but one of the assumptions of Carleman's theorem concerning the distinctness of the characteristic values of the matrix  $\|a_{ij}(x, y)\|$  for  $x = 0$ , and which possesses a solution of class  $C^\infty$  on the whole plane, vanishing together with all its derivatives for  $x = 0$ , and not vanishing identically in any neighbourhood of the point  $(0, 0)$ . The problem of the existence of such systems with coefficients of the class  $C^1$  was raised by Petrovskij [2], since in a similar example constructed by A. Myśkis [3] the derivative of the coefficients with respect to the variable  $y$  was not bounded in any neighbourhood of the point  $(0, 0)$ . In our example the functions  $a_{ij}(x, y)$  ( $i, j = 1, 2$ ) are of class  $C^\infty$  on the whole plane and the functions  $b_{ij}(x, y)$  ( $i, j = 1, 2$ ) vanish identically.

\*) This example was communicated on April 24, 1953 at the meeting of the Section of Differential Equations of the Institute of Mathematics, Polish Academy of Sciences.

In order to define the functions  $a_{ij}(x, y)$ ,  $u_q(x, y)$  ( $i, j, q = 1, 2$ ) we introduce the following notations:

$$(2) \quad A(s) = \frac{\int_0^s e^{t(t-1/4)} dt}{\int_0^{1/4} e^{t(t-1/4)} dt}$$

$$(3) \quad A_{n,k}(x) = A\left(n(n+1)x - n - \frac{k}{n}\right) \quad (n=1, 2, \dots; k=0, 1, 2, 3)$$

$$(4) \quad F_n(x, y) = \frac{(\frac{1}{3})^{n+1} e^{-2^n} A'_{n,1}(x)}{1 + \frac{1}{3} e^{-2^n} A_{n,1}(x) (\sin 3^n y \sin 3^{n+1} y - \cos 3^n y \cos 3^{n+1} y)},$$

$$(5) \quad G_n(x, y) = \frac{(\frac{1}{3})^n e^{-7 \cdot 2^n} A'_{n,3}(x)}{1 + 3 e^{-7 \cdot 2^n} (1 - A_{n,3}(x)) (\sin 3^{n+1} y \sin 3^n y - \cos 3^{n+1} y \cos 3^n y)}$$

Now let us define the functions  $a_{ij}(x, y)$ ,  $u_q(x, y)$  ( $i, j, q = 1, 2$ ) in the following manner

$$a_{ij}(x, y) = u_q(x, y) = 0 \quad \text{for } x \leq 0 \quad (i, j, q = 1, 2)$$

$$a_{11}(x, y) = a_{12}(x, y) = a_{22}(x, y) = 0, \quad a_{21}(x, y) = \frac{2A'_{n,0}(x)}{3^{n+1}}$$

$$u_1(x, y) = e^{-2^{n+1}} \cos 3^{n+1} y, \quad u_2(x, y) = (1 - 2A_{n,0}(x)) e^{-2^{n+1}} \sin 3^{n+1} y$$

for

$$\frac{1}{n+1} < x \leq \frac{1}{n+1} + \frac{1}{4n(n+1)} \quad (n=1, 2, \dots)$$

$$a_{11}(x, y) = -F_n(x, y) \sin 3^{n+1} y \cos 3^n y, \quad a_{12}(x, y) = -F_n(x, y) \cos 3^{n+1} y \cos 3^n y$$

$$a_{21}(x, y) = -F_n(x, y) \sin 3^{n+1} y \sin 3^n y, \quad a_{22}(x, y) = -F_n(x, y) \cos 3^{n+1} y \sin 3^n y$$

$$u_1(x, y) = e^{-2^{n+1}} \cos 3^{n+1} y + A_{n,1}(x) e^{-3 \cdot 2^n} \cos 3^n y,$$

$$u_2(x, y) = -e^{-2^{n+1}} \sin 3^{n+1} y + A_{n,1}(x) e^{-3 \cdot 2^n} \sin 3^n y,$$

for

$$\frac{1}{n+1} + \frac{1}{4n(n+1)} < x \leq \frac{1}{n+1} + \frac{2}{4n(n+1)} \quad (n=1, 2, 3, \dots)$$

$$a_{11}(x, y) = a_{22}(x, y) = 0, \quad a_{12}(x, y) = \frac{2 \cdot 2^n A'_{n,2}(x)}{3^n}, \quad a_{21}(x, y) = -\frac{2 \cdot 2^n A'_{n,2}(x)}{3^n},$$

$$u_1(x, y) = e^{-2^{n(2+6A_{n,2}(x))}} \cos 3^{n+1} y + e^{-2^n(3-2A_{n,2}(x))} \cos 3^n y,$$

$$u_2(x, y) = -e^{-2^{n(2+6A_{n,2}(x))}} \sin 3^{n+1} y + e^{-2^n(3-2A_{n,2}(x))} \sin 3^n y,$$

for

$$\frac{1}{n+1} + \frac{2}{4n(n+1)} < x \leq \frac{1}{n} - \frac{1}{4n(n+1)} \quad (n=1, 2, \dots)$$

$$a_{11}(x, y) = G_n(x, y) \cos 3^{n+1} y \sin 3^n y, \quad a_{12}(x, y) = -G_n(x, y) \cos 3^{n+1} y \cos 3^n y,$$

$$a_{21}(x, y) = -G_n(x, y) \sin 3^{n+1} y \sin 3^n y, \quad a_{22}(x, y) = G_n(x, y) \sin 3^{n+1} y \cos 3^n y,$$

$$u_1(x, y) = (1 - A_{n,3}(x)) e^{-3 \cdot 2^n} \cos 3^{n+1} y + e^{-2^n} \cos 3^n y,$$

$$u_2(x, y) = (A_{n,3}(x) - 1) e^{-3 \cdot 2^n} \sin 3^{n+1} y + e^{-2^n} \sin 3^n y,$$

for

$$\frac{1}{n} - \frac{1}{4n(n+1)} < x \leq \frac{1}{n} \quad (n = 1, 2, \dots)$$

$$a_{ij}(x, y) = 0 \quad (i, j = 1, 2), \quad u_1(x, y) = e^{-2} \cos 3y, \quad u_2(x, y) = e^{-2} \sin 3y \quad \text{for } 1 < x.$$

Formula (2) implies that the function  $A(s)$  is of class  $C^\infty$  for  $0 \leq s \leq \frac{1}{4}$  and  $A(0) = 0$ ,  $A(\frac{1}{4}) = 1$ ,  $0 \leq A(s) \leq 1$  for  $0 \leq s \leq \frac{1}{4}$ ,  $\frac{d^k A(s)}{ds^k} = 0$  for  $s = 0$  and  $s = \frac{1}{4}$  ( $k = 1, 2, 3, \dots$ ), hence the functions  $a_{ij}(x, y)$   $u_q(x, y)$  are of class  $C^\infty$  for  $x \neq 0$ . It is evident that the following inequalities hold:

$$\left| \frac{\partial^{k+p} u_q(x, y)}{\partial x^k \partial y^p} \right| \leq L_{kp} e^{-2^n} \cdot [n(n+1)]^k \cdot 3^{(n+1)p} 2^{kn}$$

$$\left| \frac{\partial^{k+p} a_{ij}(x, y)}{\partial x^k \partial y^p} \right| \leq M_{kp} \max [e^{-2^n} [n(n+1)]^{k+1} \cdot 3^{np}, \left(\frac{2}{3}\right)^n [n(n+1)]^{k+1}]$$

for

$$\frac{1}{n+1} < x \leq \frac{1}{n} \quad (n = 1, 2, \dots)$$

and for certain constants  $L_{kp}$ ,  $M_{kp}$  independent of  $n$ .

From these inequalities it follows that

$$\lim_{x \rightarrow 0} \frac{\partial^{k+p} u_q(x, y)}{\partial x^k \partial y^p} = \lim_{x \rightarrow 0} \frac{\partial^{k+p} a_{ij}(x, y)}{\partial x^k \partial y^p} = 0 \quad (\text{for } k, p = 0, 1, 2, \dots; i, j, q = 1, 2)$$

hence the functions  $a_{ij}(x, y)$ ,  $u_q(x, y)$  ( $i, j, q = 1, 2$ ) are of class  $C^\infty$  on the whole plane and vanish together with all their derivatives for  $x = 0$ . It can easily be verified that the functions  $a_{ij}(x, y)$ ,  $u_q(x, y)$  ( $i, j, q = 1, 2$ ) satisfy equations (1) and that the functions  $u_1(x, y)$   $u_2(x, y)$  do not vanish in any neighbourhood of the point  $(0, 0)$ . This completes the proof.

Systems with analogous properties which are either of elliptic or parabolic or hyperbolic type for  $x \neq 0$ , may be constructed by a similar method. The same applies to the construction of a similar example for an equation of second order.

Institute of Mathematics, Polish Academy of Sciences

#### REFERENCES

- [1] Carleman T., *Sur un problème d'unicité pour les systèmes d'équation aux dérivées partielles à deux variables indépendantes*, Ark. f. Mat. Astr. Fys. 26 B:17 (1939).
- [2] Petrovskii I. G., *Lektsii ob uravneniakh s častnymi proizvodnymi*, Moskva-Leningrad 1950, 53—54.
- [3] Myškis A. D., *O metode A. Haara v voprose o edinstvennosti rešenija zadaci dla sistem differencialnykh uravneni v častnykh proizvodnykh*, DAN SSSR, No. 1 58 (1947), 21—24.







## Some Inequalities between the Moments of Equivalent Random Variables

by

S. ZUBRZYCKI

*Communicated by H. STEINHAUS at the meeting of December 14, 1953*

**1. Definitions.** We say that random variables  $\xi_1, \xi_2, \dots$  are equivalent  $m$  by  $m$ , if the distribution function

$$\omega_m(a_1, a_2, \dots, a_m) = Pr(\xi_{i_1} < a_1, \dots, \xi_{i_m} < a_m),$$

with mutually different indices  $i_1, i_2, \dots, i_m$  depends only on  $m$  (cf. [1], [2], [3]). We say that the variables  $\xi_1, \xi_2, \dots$  with the finite  $m^{\text{th}}$  moments are weakly equivalent  $m$  by  $m$ , if for  $k \leq m$ , the moments

$$\mu_{s_1, s_2, \dots, s_k} = E \xi_{i_1}^{s_1} \cdot \xi_{i_2}^{s_2} \cdot \dots \cdot \xi_{i_k}^{s_k},$$

where  $s_1 + \dots + s_k = k$  and  $i_1, i_2, \dots, i_k$  are mutually different, depend only on exponents  $s_1, s_2, \dots, s_k$ . The variables  $\xi_1, \xi_2, \dots$  are weakly equivalent, if they are weakly equivalent  $m$  by  $m$  for  $m = 1, 2, \dots$

### 2. Theorems.

(i) *If the random variables  $\xi_1, \xi_2, \dots, \xi_n$  are weakly equivalent  $m$  by  $m$ , then*

$$\mu_{\underbrace{1, 1, \dots, 1}_k}^l \geq \mu_{\underbrace{1, 1, \dots, 1}_l}^k + O\left(\frac{1}{n}\right) \quad \text{for } l < k \leq m.$$

In particular, if  $m=2$ , a more precise inequality holds:

(ii) *If the random variables  $\xi_1, \xi_2, \dots, \xi_n$  are weakly equivalent 2 by 2, then*

$$\mu_{1,1} \geq \mu_1^2 - \frac{\mu_{2,0} - \mu_1^2}{n-1}.$$

It follows from (ii) that weakly equivalent (2 by 2) random variables, forming an infinite sequence, have a non-negative correlation coefficient (which is known, see [4], p. 9).

If we consider events  $E_1, E_2, \dots, E_n$  instead of random variables  $\xi_1, \xi_2, \dots, \xi_n$ , the equivalence  $m$  by  $m$  and the weak equivalence  $m$  by  $m$  are obviously logically equivalent.

The following theorem on events, more precise than (ii), holds:

(iii) *If the events  $E_1, E_2, \dots, E_n$  are equivalent 2 by 2, then*

$$\omega_2 \geq \omega_1^2 - \frac{\omega_1(1-\omega_1)}{n-1} + \frac{(n\omega_1 - [n\omega_1])(1-n\omega_1 + [n\omega_1])}{n(n-1)},$$

where  $\omega_1 = Pr(E_1)$ ,  $\omega_2 = Pr(E_1 \cdot E_2)$ , and  $[n\omega_1]$  denotes the integral part of  $n\omega_1$ .

Inequalities (ii) and (iii) cannot be sharpened. This results from the following proposition:

(iv) *For every  $\omega_1$  there is a system  $E_1, E_2, \dots, E_n$  of equivalent events for which the equality sign holds in formula (iii).*

**3. Application.** Theorem (iii) possesses an interpretation in the method of investigating the composition of meadows by Levy's ruler (cf. [5]). It is one metre long and provided with nails. We cast it at random on a meadow and compute the number of nails which touch particular types of plants. From theorem (iii) we may conclude that the probability of the event that two particular nails indicate the same type of plant in a meadow having only two kinds, is at least  $\frac{1}{3}$ . This can be formulated more precisely as follows:

Let  $R$  be a plane Lebesgue measurable set such that for every point  $(x, y)$ , the points  $(x, y)$ ,  $(x+1, y)$  and  $(x, y+1)$  belong or do not belong to  $R$  simultaneously. Let  $\omega_1$  denote the measure of the part of  $R$  contained in the unit square. Let us denote by  $\Omega$  the cube

$$E_{(x,y,\varphi)} \{0 < x < 1, 0 < y < 1, 0 < y < 2\pi\}$$

and let us consider in  $\Omega$  a product measure  $||$  such that  $|\Omega| = 1$ .

Let  $AB$  be a moving segment with centre  $S$  and length  $2r$ . Denoting by  $x, y$  the coordinates of  $S$  and by  $\varphi$  the angle between the  $x$ -axis and the vector  $\vec{SA}$ , we may write  $A = A(x, y, \varphi)$ ,  $B = B(x, y, \varphi)$ .

Finally, setting

$$\psi(\omega_1) = \begin{cases} 1-2\omega_1 & \text{for } 0 \leq \omega_1 \leq \frac{1}{3}, \\ \frac{1}{3} & \text{for } \frac{1}{3} \leq \omega_1 \leq \frac{2}{3}, \\ 2\omega_1-1 & \text{for } \frac{2}{3} \leq \omega_1 \leq 1, \end{cases}$$

we obtain the following inequality:

$$\begin{aligned} & \left| E_{(x,y,\varphi) \in \Omega} \{A(x,y,\varphi) \in R \text{ and } B(x,y,\varphi) \in R\} \right| \\ & + \left| E_{(x,y,\varphi) \in \Omega} \{A(x,y,\varphi) \notin R \text{ and } B(x,y,\varphi) \notin R\} \right| \geq \psi(\omega_1). \end{aligned}$$

# REFERENCES

- [1] Finetti B. de, *Funzione caratteristica di un fenomeno aleatorio*, Mem. R. Acc. Naz. Lincei. 6 ser., **4** (1930), 86.
- [2] — *Classi di numeri aleatori equivalenti*, Atti R. Acc. Naz. Lincei **18** (1933), 107—110.
- [3] Dynkin E. B., *Klasy ekvivalentnykh slučajnykh vieličin*, Usp. Matem. Nauk **8.2** (1953), 125—130.
- [4] Milicer-Grużewska H., *O współczynniku korelacji a posteriori zmiennych ekwivalentnych* (*The coefficient of correlation a posteriori of equivalent variables*), Comptes Rendus de la Société des Sciences et des Lettres de Varsovie, Cl. III, **39** (1946), 1—17 (especially p. 9).
- [5] Levy E. B., *The Point Methods of Pasture Analysis*, New Zealand Journal of Agriculture **46** (1933).





# The Influence of Hindered Rotation on the Scattering of Slow Neutrons by Bound Protons

by

W. KOŁOS

*Communicated by L. INFELD at the meeting of October 19, 1953*

The cross section of a bound proton for the scattering of slow neutrons may be calculated by assuming the interaction potential between neutron and proton to be in the form of a delta-function and by using Born's first approximation ([1] and [2]). In this approximation the differential cross section of the proton is given by

$$(1) \quad d\sigma_{f,i} = \frac{k_f \mu^2 \sigma_0}{k_i \pi} \left| \int \exp \{ i(\vec{k}_i - \vec{k}_p) \cdot \vec{r}_n \} U_i(\vec{r}_p) U_f^*(\vec{r}_p) \delta(\vec{r}_n - \vec{r}_p) dv_n dv_p \right|^2 d\Omega,$$

where  $U_i(\vec{r}_p)$  and  $U_f(\vec{r}_p)$  are the eigenfunctions of the proton in the initial and final states respectively,  $\vec{r}_n$  and  $\vec{r}_p$  denote the coordinates of the neutron and proton respectively,  $\sigma_0$  is the cross section of a free proton,  $\mu = M_{mol}/(M_n + M_{mol})$ ,  $\vec{k}_i$  and  $\vec{k}_f$  are the wave vectors of the neutron before and after collision respectively. The difference between neutron and proton mass is neglected.

The molecule in which the proton is bound is assumed to be a symmetric rotator which has an additional degree of torsional freedom between two of its principal parts. The motion of such a molecule is best described by means of the Eulerean angles  $\theta, \psi, \varphi_1, \varphi_2$  where  $\theta$  denotes the angle between the space-fixed axis  $z$  and the axis of symmetry  $x'$  of the molecule  $\psi$  is the angle between the line of nodes and the  $x$  axis,  $\varphi_1$  and  $\varphi_2$  are the angles between the line of nodes and the  $x''$  and  $x'''$  axes fixed in the lower and upper parts of the molecule respectively.

We assume the hindering potential to be in the form:

$$(2) \quad V = \frac{H}{2} (1 - \cos n\varphi')$$

where  $H$  is the height of the barrier,  $\varphi'$  is the angle of rotation between one part of the molecule and another, and  $n$  is the number of minima of

the potential energy curve as  $\varphi'$  increases from zero to  $2\pi$ . The potential function given above is one of the simplest of those having both the desired flexibility and the necessary properties of symmetry.

By introducing new variables defined by

$$(3) \quad \begin{aligned} \varphi' &= \varphi_1 - \varphi_2 \\ \varphi &= \beta_1 \varphi_1 + \beta_2 \varphi_2 \end{aligned}$$

where

$$\beta_i = \frac{A_i}{A_1 + A_2} \quad (i = 1, 2)$$

and  $A_i$  is the moment of inertia of either the first or second part of the molecule about the axis of internal rotation, the Schrödinger equation of the rotator was found to be separable [5]. The eigenfunctions we then get in the form:

$$(4) \quad \Psi_{m\varrho}(\theta, \psi, \varphi, \varphi') = \frac{1}{\sqrt{2\pi}} U_m(\theta, \psi, \varphi) M_{\varrho m}(\varphi'),$$

where  $\varrho$  is the quantum number of the hindered rotation,  $m$  denotes a set of quantum numbers  $(\tau, \tau', j)$  describing the rotation of a rigid molecule,  $U_m(\theta, \psi, \varphi)$  is the normalized wave function of a rigid symmetric rotator

$$(5) \quad U_m(\theta, \psi, \varphi) = C'_m \Theta_m(\theta) e^{i(\tau\varphi + \tau'\psi)}$$

$M_{\varrho m}(\varphi')$  is the Mathieu function of the form:

$$(6) \quad M_{\varrho m}(\varphi') = e^{-i\tau\beta_1\varphi'} \sum_{n=-\infty}^{\infty} a_n^{(\varrho\tau)} e^{in\varphi'}.$$

The  $z$ -component of the radius vector of the proton whose rotation is described by the angle  $\varphi_2$ , written in terms of the Eulerean angles will be

$$(7) \quad z = c \cos \theta + a \sin \theta \sin(\varphi - \beta_1 \varphi').$$

Having integrated in (1) over the coordinates of the neutron, we chose a coordinate system with  $z$  axis in the direction of  $\vec{K} = \vec{k}_i - \vec{k}_f$  and using (7) and (4) with (5) and (6) we get

$$(8) \quad \begin{aligned} d\sigma_{m_f \varrho_f m_i \varrho_i} &= \frac{k_f \mu^2 \sigma_0}{k_i \pi (2\pi)^2} C_{m_i}^2 C_{m_f}^2 \left| \sum_{n=-\infty}^{+\infty} b_n \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \right. \\ &\exp \{ iK [c \cos \theta + a \sin \theta \sin(\varphi - \beta_1 \varphi') \\ &\quad + i(\tau_i - \tau_f)\varphi + i(\tau'_i - \tau'_f)\psi - i(\tau_i - \tau_f)\beta_1 \varphi' + in\varphi'] \\ &\quad \left. \Theta_{m_i}(\theta) \Theta_{m_f}^*(\theta) \sin \theta d\theta d\psi d\varphi d\varphi' \right|^2 d\Omega \end{aligned}$$

where

$$(9) \quad b_n = \sum_{m=-\infty}^{+\infty} a_m^{(e_i \tau_i)} a_{m-n}^{(e_f \tau_f)}.$$

Changing the integration variables:

$$(10) \quad \varphi - \beta_1 \varphi' = \vartheta, \quad \varphi' = \vartheta'$$

and integrating over  $\vartheta'$  we get from the series in (8) the only non-vanishing term for  $n=0$

$$(11) \quad d\sigma_{m_f m_i e_i} = b_0^2 \frac{k_f \mu^2 \sigma_0}{k_i \pi} C_{m_i}^2 C_{m_f}^2 \left| \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \exp \{ iK(c \cos \theta + a \sin \theta \sin \vartheta) + i(\tau_i - \tau_f) \vartheta + i(\tau_i' - \tau_f') \vartheta' \} \Theta_{m_i}(\theta) \Theta_{m_f}^*(\theta) \sin \theta d\theta d\vartheta d\vartheta' \right|^2 d\Omega.$$

From (11) we see at once that the calculated cross section is equal to the cross section of a proton bound with a rigid rotating molecule, multiplied by  $b_0^2$ .

It may be shown that for the proton bound with the other part of the molecule whose rotation is described by the angle  $\varphi_1$ , the result obtained above is also valid, but in this case  $b_0$  when written in terms of the same  $a_n$  will have the form:

$$(12) \quad b_0 = \sum_{m=-\infty}^{\infty} a_m^{(e_i \tau_i)} a_{m-(\tau_i-\tau_f)}^{(e_f \tau_f)}.$$

For the total cross section the integration over the full solid angle gives an analogous relation:

$$(13) \quad \sigma_{m_f m_i e_i} = b_0^2 \sigma_{m_f m_i}$$

where  $\sigma_{m_f m_i}$  is the cross section of a proton bound in a rigid rotating molecule.

The wave function  $\Psi_{m_0}$  given by (4) is so normalized that we have

$$(14) \quad \sum_{n=-\infty}^{\infty} (a_n^{(e_i \tau_i)})^2 = 1, \quad \sum_{n=-\infty}^{\infty} (a_n^{(e_f \tau_f)})^2 = 1,$$

which, according to Cauchy's inequality, gives

$$(15) \quad b_0 = \sum_{n=-\infty}^{\infty} a_n^{(e_i \tau_i)} a_n^{(e_f \tau_f)} \leq 1.$$

From (14) and (15) we see at once that the cross section for collisions in which neither hindered rotation nor rotation of the whole molecule about the axis of hindered rotation is excited, will be the same as for a rigid

molecule, but for collisions in which the latter is excited we shall obtain a cross section smaller than that of a rigid molecule.

The theory given above explains the disagreement found by Janik (1953) between the cross section of a methyl alcohol molecule obtained experimentally and that calculated from the simplified theory of Sachs and Teller (1941).

$$\sigma_{\text{exp}} = 180 \cdot 10^{-24} \text{ cm}^2; \quad \sigma_{\text{theor}} = 231 \cdot 10^{-24} \text{ cm}^2.$$

The coefficients  $b_0^2$  in this case may be obtained by using the values of  $\alpha_n$  calculated by Koehler and Dennison (1940). See Table I.

TABLE I

Transition $\tau_i \leftrightarrow \tau_f$	$0 \leftrightarrow 1$	$0 \leftrightarrow 4$	$0 \leftrightarrow 6$	$0 \leftrightarrow 8$	$0 \leftrightarrow 10$	$0 \leftrightarrow 12$	$2 \leftrightarrow 12$	$6 \leftrightarrow 14$	$0 \leftrightarrow 1$	$0 \leftrightarrow 2$	$0 \leftrightarrow 5$
$b_0^2$	0.99	0.94	0.88	0.82	0.73	0.64	0.72	0.82	0.94	0.83	0.32
	For the proton bound in the $\text{CH}_3$ group							For the proton bound in OH			

In the case of a methyl alcohol molecule the energy of thermal neutrons is sufficient to excite the higher "multipole" transitions, and as the neutron wave length is of the same order of magnitude as the molecular dimensions we may expect a relatively great probability for such transitions.

However, from Table I we see that  $b_0^2$  approaches unity with decreasing  $|\tau_i - \tau_f|$ , so we may expect that the cross section of a proton bound in a molecule such as  $\text{CH}_3\text{OH}$ , will depend to a great extent on the energy of the neutrons and on the thermal energy of the scattering molecules (this latter dependence being due to the collisions associated with de-excitations of the proton). The diminishing of the cross section caused by hindered rotation is less when both the energy of the neutrons and the thermal energy of the scattering molecules decrease, and when they approach zero we obtain the same cross section as for a rigid molecule. We cannot conclude from the experiments so far published that the effect described above really exists. So I am indebted to J. A. Janik for his promise to carry out the necessary measurements which would make it possible to check the theory.

The coefficients  $b_0^2$  given in Table I are calculated, assuming the height of the potential barrier as being  $H = 769 \text{ cm}^{-1}$ . However, using recently published spectroscopical data, Ivash and Dennison have found it to be  $H = 374.8 \text{ cm}^{-1}$  [7]. The coefficients  $b_0^2$  calculated with this new value of the potential barrier will be smaller than those given in Table I. E. g. for the proton bound in the  $\text{CH}_3$  group we shall have:

$\tau_i \leftrightarrow \tau_f$	$0 \leftrightarrow 1$	$0 \leftrightarrow 4$	$0 \leftrightarrow 7$	$0 \leftrightarrow 10$
$b_0^2$	0.99	0.92	0.80	0.63



I should like to express my sincere thanks to Professor L. Infeld for his kind interest in this work, and to J. Werle for many valuable and helpful discussions.

Institute of Theoretical Physics, University of Warsaw

#### REFERENCES

- [1] Breit G., Phys. Rev. **71** (1947), 215.
- [2] Fermi E., Ric. Scient. **7** (1936), 13.
- [3] Janik J. A., Acta Phys. Pol. **12** (1953), 45; Bull. Acad. Pol. Sc., Cl. III, **1** (1953), 45.
- [4] Koehler J. S. and Dennison D. M., Phys. Rev. **57** (1940), 1006.
- [5] Nielsen H. H., Phys. Rev. **40** (1932), 445.
- [6] Sachs R. G. and Teller E., Phys. Rev. **60** (1941), 18.
- [7] Ivash and Dennison, J. Chem. Phys. **21** (1953), 1804.



## Sind elektrische Oktupollinien im Röntgenspektrum beobachtbar?

von

L. MAURIN

Vorgelegt von W. RUBINOWICZ in der Sitzung am 19. Oktober 1953

In dieser Note wurden die Intensitäten der elektrischen Oktupollinien in der  $K$ -,  $L$ - und  $M$ -Serie des Röntgenspektrums berechnet, um die Frage zu entscheiden, bei welchen Elementen diese Linien beobachtbar sind.

Die Rechnungen wurden dabei nur für diejenigen Übergänge durchgeführt, wo die Oktupollinie die Ergänzung eines Dipollinienmultipletts bildet, da hier die günstigsten Beobachtungsmöglichkeiten bestehen. Für die übrigen Oktupollinien werden die Intensitäten später angegeben werden.

Behandelt man das Problem als ein Ein-Elektronenproblem und zieht nur die Übergänge in Betracht, die mit der Änderung der azimuthalen Quantenzahl  $l=2 \rightarrow l=1$  verbunden sind, so erhält man für die Intensitäten der Oktupollinien in nicht relativistischer Näherung den Ausdruck [1]:

$$(1) \quad W_3^{el}(n, n') = 3 \cdot 2^{-28} \cdot Z^{10} \cdot \alpha^4 K L C_n^{n'} (D_n^{n'})^2.$$

Dabei bedeuten:

- $W_3^{el}(n, n')$  die Intensität der elektrischen Oktupollinie,  
 $n$  und  $n'$  die Hauptquantenzahlen des Anfangs-bzw. Endzustandes,  
 $\alpha$  die Sommerfeldsche Feinstrukturkonstante,  
 $K = \frac{(2\pi R)^4}{3} c \left( \frac{e\hbar^2}{m_0 c^2} \right)^2 2^{10} = 14.939 \text{ erg/sec. und}$   
 $L$  den Ausdruck:

$$(2) \quad L = \frac{4}{3 \cdot 1^2 \cdot 3^2 \cdot 5^2 \cdot 7} \sum_{\mu=-3}^{+3} \sum_{m=-2}^{+2} \frac{(3-\mu)!}{(3+\mu)!} \{A_{\mu m}^{3m+\mu}\}_2^2,$$

wo  $\mu = m' - m$  ( $m$  = magnetische Quantenzahl) und

$$A_{\mu m}^{3m+\mu} = \frac{1}{\sqrt{N_{lm} N_{l'm'}}} \int_0^\pi P_2^m P_\lambda^{m+\mu} P_\gamma^\mu \sin \vartheta d\vartheta.$$

- $P_n^\mu$  bezeichnet hier eine Kugelfunktion in der Neumannschen Normierung und  
 $N_{l,m}$  den Normierungsfaktor.  
 $C_n^{\mu'}$  ist in (1) gleich dem Ausdruck:

$$(3) \quad C_n^{\mu'} = \frac{n^2 - n^{12}}{(n')^{22} n^{24}} \frac{(n-3)! (n'-2)!}{[(n+2)!]^3 [(n'+1)!]^3}$$

und  $D_n^{\mu'}$  gleich dem Integral

$$(4) \quad D_n^{\mu'} = \int_0^\infty s^8 L_{n+2}^5 \left( \frac{1}{n} s \right) L_{n'+1}^3 \left( \frac{1}{n'} s \right) e^{-\frac{1}{2}s \left( \frac{1}{n} + \frac{1}{n'} \right)} ds$$

( $L_s^t$  ist ein Laguerresches Polynom). Nach Gaunt [2] gilt dabei

$$(5) \quad \int_{-1}^{+1} P_l^{\nu+w} P_m^\nu P_n^w d\xi = (-1)^{p-m-w} \cdot \frac{2(m+\nu)! (n+w)! (l+m-n)! p!}{(m-\nu)! (p-l)! (p-n)! (2p+1)!} \\ \cdot \sum_k \frac{(-1)^k}{k!} \frac{(l+\nu+w+k)!}{(l-\nu-w-k)!} \frac{(m+n-\nu-w-k)!}{(m-n+\nu+w+k)! (v-w-k)!},$$

$$\text{wo } p = \frac{l+m+n}{2}.$$

In (5) ist die Summe über diejenigen  $k$  zu erstrecken, für die dieser Ausdruck sinnvoll ist (d. h. wo keine Fakultäten negativer ganzer Zahlen auftreten).

Auf diese Weise erhalten wir:

$$(6) \quad L = \frac{8}{3675}.$$

Nach Schrödinger [3] ist

$$(7) \quad \int_0^\infty x^p e^{-\frac{\alpha+\beta}{2}x} L_{n+k}^n(\alpha x) L_{n'+k'}^{\mu'}(\beta x) dx \\ = \left( \frac{2}{\alpha+\beta} \right)^{p+1} \sum_{\lambda=0}^k \sum_{\mu=0}^{k'} (-1)^\mu \frac{\gamma^{\lambda+\mu}}{\lambda! \mu!} \int_0^\infty y^{p+\lambda+\mu} L_{n+k}^{n+\lambda} L_{n'+k'}^{\mu'+\mu} e^{-y} dy, \\ (8) \quad \int_0^\infty y^{p+\lambda+\mu} L_{n+k}^{n+\lambda} L_{n'+k'}^{\mu'+\mu} e^{-y} dy \\ = s! (t+u)! (\nu+w)! \sum_{\tau=0}^{\leq uw} (-1)^{\tau+u+\nu+w} \binom{s-t}{u-\tau} \binom{s-\nu}{w-\tau} \binom{-s-1}{\tau}$$



und

$$\gamma = \frac{\alpha - \beta}{\alpha + \beta},$$

wobei

$$t = n + 1 \quad u = k - \lambda \quad v = n' + \mu \quad w = k' - \mu \quad s = p + \lambda + \mu.$$

Auch in (8) ist die Summe nur über solche  $\lambda$  zu erstrecken, für die sie sinnvoll ist.

Im Falle  $k=0$  oder  $k'=0$  nehmen die Integrale (7) und (8) eine sehr einfache Gestalt an, andernfalls können sie als lineare Kombinationen der Integrale dargestellt werden, für die  $k=0$  oder  $k'=0$  ist.

Für die  $L$ -Serie ( $n=2$ ) erhalten wir daher:

$$D_n^2 = -4^{11} 3! n^{10} \frac{(n-2)^{n-6} (n+4) (n-4)}{(n+2)^{n+6} (n-3)!} [(n+2)!]^2.$$

Schliesslich wird

$$(9) \quad W_3^{el}(n, 2) = LK\alpha^4 Z^{10} \cdot \frac{(n^2 - 16)^2 (n^2 - 1)}{n^3} \cdot \frac{(n-2)^{2n-8}}{(n+2)^{2n+8}}.$$

(9) ist nur für  $n \geq 6$  gültig, wie aus der Berechnung dieses Ausdruckes folgt. Die ausgerechneten Intensitäten für  $n < 6$  sind in der unten angegebenen Tabelle zusammengestellt.

Im Falle  $n=4$  haben wir  $W_3^{el}(4, 2) = 0$ , da  $D_4^2 = 0$ , d. h.

$$\int_0^\infty R_{42} R_{21} (kr)^3 r^2 dr = 0.$$

Das Verschwinden des obigen Integrals kann man als einen Beweis für die Existenz einer Auswahlregel für die Hauptquantenzahl ansehen, die allerdings nur für einen speziellen Wert dieser Quantenzahl wirksam ist.

Ähnlich berechnet man die Intensitäten für die elektrische Oktupolstrahlung der Spektrallinien in der  $M$ -Serie. Für  $n \geq 7$  wird

$$(10) \quad W_3^{el}(n, 3) = KL\alpha^4 Z^{10} 3^2 2^5 \frac{(n^2 - 4) (n^2 - 1) (n - 30)^2 (n - 3)^{2n-4}}{n^3 (n + 3)^{2n+4}}.$$

Die übrigen Intensitäten ( $n < 7$ ) sind in der nachstehenden Tabelle zusammengestellt.

TABELLE

Anfangszustand	Endzustand			
	$2 p_{1/2}(I_{II}) [n'=2, l'=1]$		$3 p_{1/2}(M_{II}) [n'=3, l'=1]$	
	$W_3 Z^{10}$ erg/sec.	$\bar{v} Z^{-1}$ cm. <sup>-1</sup>	$W_3 Z^{10}$ erg/sec.	$\bar{v} Z^{-1}$ cm. <sup>-1</sup>
$3 d_{3/2}(N_V)$ [ $n=3, l=2$ ]	$2.057 \cdot 10^{-15}$	$15242 + Z^2 \cdot 0.438$		
$4 d_{3/2}(N_V)$ [ $n=4, l=2$ ]	0		$6.5307 \cdot 10^{-16}$	$5334.6 + Z^2 \cdot 0.151$
$5 d_{3/2}(O_V)$ [ $n=5, l=2$ ]	$3.238 \cdot 10^{-17}$	23045	$5.1027 \cdot 10^{-16}$	$78037 + Z^2 \cdot 154$

Die experimentellen Methoden erlauben die Intensitäten von Spektrallinien zu messen, die circa  $10^4$  mal kleiner sind als die der hellsten Dipollinien. Im Spektrum des Platins wurde zum Beispiel eine Spektrallinie beobachtet, die etwa  $10^4$  mal schwächer als die  $\beta_1$  Linie ist (Übergang  $3d_{3/2} \rightarrow 2p_{1/2}$ ) [4]. Die berechnete Intensität dieser Linie beträgt [5]

$$3.2 \cdot 10^{-4} Z^6,$$

wo  $Z$  die Ordnungszahl bedeutet.

Da die Intensität der elektrischen Oktupolstrahlung zu  $Z^{10}$  proportional ist, können wir  $W_3^{el} = W_3' Z^{10}$  setzen. Für das Verhältnis der Intensität einer Oktupollinie zur Intensität der  $\beta_1$  Linie des Platins erhalten wir somit

$$\frac{W_3' Z^{10}}{3.2 \cdot 10^{-4} Z^6} \geq 10^{-4} \quad \text{wenn} \quad W_3' = \frac{3.2 \cdot 10^{-8}}{Z^4}.$$

Da  $0 < Z \leq 92$  so wird  $W_3' \geq 5.01 \cdot 10^{-16}$ . Daher können unter den hier berechneten Intensitäten nur diejenigen der Linien messbar sein, die den Übergangen:  $3.2 \rightarrow 2.1$ ;  $4.2 \rightarrow 3.1$ ;  $5.2 \rightarrow 3.1$  entsprechen.

Die kleinste Atomzahl, für welche die Intensität der entsprechenden Linie messbar ist, wird durch

$$Z_{\min} \sim \frac{0.32 \cdot 10^{-8}}{W_3'}$$

gegeben.

Für die Linie  $3.2 \rightarrow 2.1$  erhalten wir also  $Z_{\min} = 63$

„ „ „  $4.2 \rightarrow 3.1$  „ „ „  $Z_{\min} = 84$

„ „ „  $5.2 \rightarrow 3.1$  „ „ „  $Z_{\min} = 89$ .

Keine Spektrallinie, deren Intensität hier angegeben wurde, konnte bisher beobachtet werden mit Ausnahme der Spektrallinie  $N_V \rightarrow L_{II}$ . Diese im Bismut-Spektrum beobachtete Linie muss aber einem erzwungenen Übergang entsprechen, da ihre Intensität nach der vorher angegebenen „Auswahlregel“ in nicht relativistischer Näherung verschwindet.

Institut für theoretische Physik III der Universität Warschau

#### LITERATUR

- [1] Blaton J., Acta Phys. Pol. **6** (1937), 256.
- [2] Gaunt, Phil. Trans. of the Roy. Soc. A. **228**, (1929), 192.
- [3] Schrödinger, Ann. der Phys. IV. **80**, (1926), 485.
- [4] Lindh A. E., Handb. d. Exp. Phys. **24/2**, 275.
- [5] Bethe, Handb. d. Phys. **24/1**, 445 und 450.

## The Expansion of Iron Spirals as a Result of Saturation with Cathodic Hydrogen

by

M. ŚMIAŁOWSKI and Z. SZKLARSKA-ŚMIAŁOWSKA

*Communicated by M. ŚMIAŁOWSKI at the meeting of October 19, 1953.*

As was shown in previous papers [1], [2], a cathode in the form of a fine iron wire becomes elongated when subjected to the internal pressure caused by penetration of atomic hydrogen into the metal. It was estimated, on the basis of the extent of the plastic deformation of the wire, that, in the presence of poisons retarding the process of molecule formation from H atoms, the pressure of hydrogen within the metal may rise to approximately 1400 atmospheres, a fact which indicates the presence of pressures of at least this same order on the surface of a working cathode. This observation seems to throw new light on the mechanism of electrodic processes and particularly on the essential nature of hydrogen overvoltage, which is the subject of much discussion among supporters of the theory of inhibited ionic discharge [3] and among those who uphold other theories, such as, for example, the adsorption hypothesis [4]. It was therefore considered necessary to make every effort towards improving the methods of investigation used hitherto and to take more advantage of the experimental data available on this subject.

It was affirmed, in the course of further research work into the behaviour of iron cathodes during electrolysis of sulphuric acid solutions, that a fine wire or iron band, bent in the shape of the letter C, expands under the influence of the penetration of atomic hydrogen in a manner similar to that of Bourdon's manometric tubes. As a result of high pressure arising in the interior inter-crystalline or intra-crystalline spaces of the material of the iron cathode, forces are created which tend to increase the curvature radius of the bent cathode. The action of these forces can only be observed in the case of elements small in thickness and in the case of metal which has been softened by heating and which possesses a sufficiently great capacity for plastic deformation. This effect may be multiplied by using a cathode of wire, bent so as to form a flat or cylindrical spiral.

Fig. 1 shows the apparatus used for examining the influence of electrolytic conditions and of various kinds of catalytic poisons upon the straightening of the iron spiral. In this drawing Fe represents the examined spiral, acting as a cathode in a 1N solution of sulphuric acid. The lower end of the spiral was charged with a glass weight,  $g$ , which in the solution weighed about 4 grams. The coils of the spiral had an initial diameter of 22 mm.;

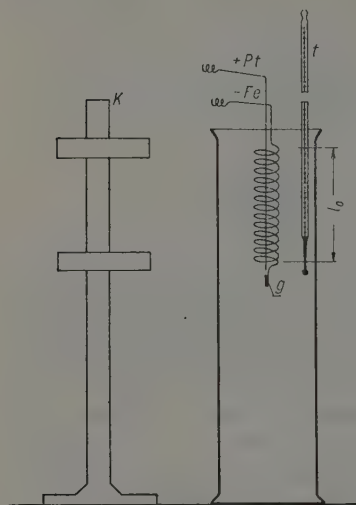


Fig. 1

the number of coils in the experiments on the influence of arsenic concentration amounted to  $s=14$ , the initial length of the spiral immersed in acid was  $l_0=50$  mm., and the total length of iron wire coiled into the spiral was  $L=1000$  mm. In the experiments on the action of different catalytic poisons, the adequate values were as follows:  $s=7$  coils,  $l_0=25$  mm.,  $L=500$  mm. Under the influence of cathodic polarisation when poisons were present, the curvature radius of each separate coil of the iron wire increased slightly and this brought about a corresponding lengthening of the whole spiral; the changes in length of the spiral were measured by a cathetometer  $K$ . As an anode we used either a simple platinum wire Pt, 1 mm. in diameter, placed in

the axis of the iron spiral, as shown in Fig. 1, or a platinum net surrounding the spiral. The way in which the anode was inserted did not affect the measurements.

Experiments were carried out on a steel wire, 0.45 mm. in diameter, taken from the same coil from which samples were taken for the experiments described in a previous paper [2].

After a suitable number of spirals had been wound from this wire, they were heated together in a hydrogen atmosphere for 30 minutes in a temperature of  $900^\circ$  for the purposes of recrystallisation, the withdrawal of all tensions, and the freeing of the surface from all organic substances. Each spiral was used only once.

First of all we examined the influence of temperature changes (ranging from  $15^\circ$  to  $50^\circ$ ) on the length of a spiral not subjected to polarisation and immersed in distilled water. In these conditions no measurable effects were noted. It was also found that a spiral does not suffer deformation when subjected to cathodic polarisation in a solution of pure sulphuric acid. On the other hand, if electrolysis takes place in the presence of some of the elements belonging to groups V and VI of the periodic system, which



are known for their capacity to poison contact catalysers, there is rapid elongation of the spiral. This process can frequently be seen with the naked eye, and sometimes the elongation amounts to as much as 1000% of the original length of the spiral. These effects are irreversible. It was found that the magnitude of the change in the length of the spiral,  $\Delta l$ , when saturated with cathodic hydrogen — a magnitude which must, without doubt, persist in a quantitative relationship with the grade of internal pressure of the gas accumulated in the structure of the metal — became established in each succeeding experiment with satisfactory reproducibility and that, on the basis of measurements of the changes in length of the spiral, it is possible to obtain a clear picture of the progress of hydrogen diffusion.

Fig. 2 gives, by way of example, the results of some observations on the elongation of spirals with number of coils  $s=14$ , which were saturated with hydrogen at a temperature of  $20^\circ$  with a current density of  $0.018 \text{ amp./cm.}^2$  in a solution  $1 \text{ N H}_2\text{SO}_4$  with the addition of  $\text{As}_2\text{O}_3$  in different concentrations. On the horizontal axis, time is marked off in minutes, starting from the commencement of electrolysis, and on the vertical axis the observed elongation of the spiral,  $\Delta l$ , in millimetres. Each value of As concentration, expressed in milligrams per litre of solution, is written against the corresponding time-elongation curve. It appears from the course of these curves that an increase of As concentration (ranging from  $0.0015 \text{ mg./l.}$  to  $3 \text{ mg./l.}$ ) causes a marked speeding-up of the uncoiling of the spiral and the attainment of a greater ultimate value of  $\Delta l$ , corresponding in given conditions to a maximal impregnation of the wire with hydrogen.

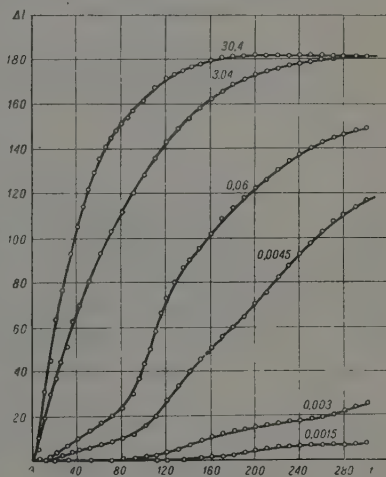


Fig. 2

Fig. 3 shows how the ultimate values of  $\Delta l$  depend on the As concentration (logarithmic scale c, expressed in grams per litre) when the same physical conditions exist as were given above for Fig. 2. From this diagram it can be seen that an increase of As concentration in the solution above a certain critical amount (about 0.1 milligrams per litre) does not cause any further increase in the ultimate value of  $\Delta l$ .

Fig. 4 shows how the ultimate values of  $\Delta l$ , corresponding to impregnation of iron spirals with cathodic hydrogen, depend on the atomic number,  $Z$ , of the elements from groups V and VI of the periodic system which were used by us as poisons. The measurements for Fig. 4 were made on spirals with number of coils  $s=7$ . The cathodic current density amounted

to 0.036 amp./cm.<sup>2</sup>, and the temperature to 20°; the concentration of the admixtures in 1 N H<sub>2</sub>SO<sub>4</sub>, in the case of all the examined elements, was greater than the critical amount (see Fig. 3). Bismuth, selenium, tellurium and antimony were added in the form of oxides, sulphur in the form of hydrogen

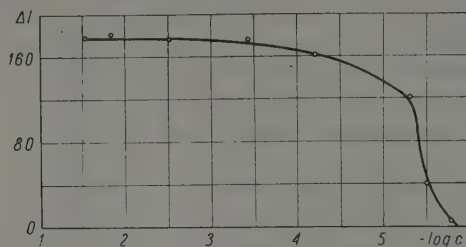


Fig. 3

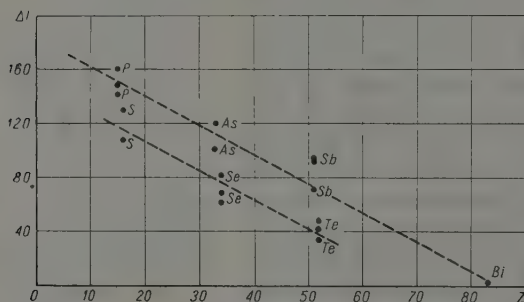


Fig. 4

sulphide, and phosphorus in the form of hydrogen phosphide. Neither the ion  $\text{SO}_4^{--}$  nor  $\text{PO}_4^{--}$  causes penetration of hydrogen atoms into the iron cathode.

The results obtained in the course of the present work confirm the view that during electrolysis there must be a high degree of hydrogen pressure on the surface of the cathode. In the presence of substances which diminish the rate of the reaction  $2\text{H} \rightarrow \text{H}_2$ , hydrogen in its atomic form plays an important part in causing this pressure, and this is the reason for the penetration of this gas into the metal cathode.

#### REFERENCES

- [1] Śmiałowski M. and Szklarska-Śmiałowska, Z., Bull. Acad. Pol. Sc., Cl. III, **1** (1953), 159.
- [2] Śmiałowski M. and Szklarska-Śmiałowska Z., Bull. Acad. Pol. Sc., Cl. III, **1** (1953), 327.
- [3] Frumkin A. N., Jofa Z. A. and Wagocki W. S., Journ. fiz. Chim. **25** (1953), 1117.
- [4] Koboziev I. I., Journ. fiz. Chim. **26** (1952), 112.

## The Critical State of Negative Azeotropes I. System of Acetic Acid-Pyridine

by

W. ŚWIĘTOSŁAWSKI and A. KRĘGLEWSKI

*Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of December 14, 1953*

### 1. Introductory remarks

Recently, one of us [1] suggested classifying the non-aqueous, negative azeotropes and proposed that they should be divided into three groups, the division depending on the differences in the nature of the attractive forces acting between the molecules of the two components. Mixtures of a weak organic acid and a weak base constitute the second group of this classification. None of the azeotropes of this group has ever been examined in its critical state.

Up to this time two negative azeotropes of the first group have been examined, one composed of dimethyl ether and hydrogen chloride, the other of carbon dioxide and acetylene. As regards the first azeotrope, Kuenen [2] found that a chemical reaction took place when it was heated to 100°C. However, extrapolation of the data obtained in the region of lower temperatures, has shown that a negative azeotrope exists also in the critical region. As regards the second negative azeotrope, Dewar [3] reported that a mixture composed of approximately equal volumes of acetylene and carbon dioxide could be liquefied at 41°C. This proved that the formation of a negative azeotrope could take place. No other negative azeotropes, besides these two, have ever been found.

The object of this paper is to answer the question as to whether or not acetic acid and pyridine can form a negative azeotrope in the critical state. Its existence under atmospheric pressure has been known for some time [4].

### 2. Description of experiment

We used pyridine, purified by fractional distillation. Its boiling temperature was equal to  $115.05 \pm 0.03^\circ$  at 755 mm. Hg.

High-grade acetic acid was refluxed with a small amount of acetic anhydride and submitted to fractional distillation. The main fraction (con-

densation temperature ranging from 118.1 to 118.3 at 755 mm. Hg) was collected and recrystallized many times. The melting temperature was found to be  $16.60 \pm 0.03^\circ \text{C}$ .

Dried capillary tubes, 15 cm. long, were weighed, filled with the required amounts of the components, then weighed again and sealed under vacuum. The loss of liquid through partial evaporation during the evacuation of air was negligible compared with the total amount of liquid in the tube. The latter, together with a standard thermometer, was placed in a large block made of duraluminium and then heated electrically\*).

When heated for a relatively long period of time, pyridine and mixtures of it with acetic acid became yellowish. The critical temperatures of these mixtures underwent changes when heated for 2–3 hours above  $300^\circ \text{C}$ . To avoid, as far as possible, decomposition of the liquid, the thermostat was heated in advance to the desired temperature, and afterwards the tubes with the liquid were put into it. The disappearance of the meniscus at the temperature  $T_m$  was observed just 15 to 30 minutes after the tubes had been placed in the thermostat. In this way the temperature  $T_m$  could be determined to within  $\pm 0.05^\circ$ . When mixing the contents of the tube, the temperature at which maximum opalescence and disappearance of the meniscus occurred, could easily be observed. No attempts were made to examine the precritical region of the mixture under investigation. For this reason the absolute value of the critical temperature could vary between  $\pm 0.2 - 0.3^\circ \text{C}$ .

### 3. Results and discussion

The results are given in the Table and in Fig. 1, in which the symbols  $k, w, r$  correspond to the disappearance of the meniscus in the middle of the tube ( $k$ ), in its upper part ( $w$ ) and in the lower part ( $r$ ), respectively.

TABLE

Tube No.	Degree of Filling	Substance	$T_m$ $^\circ \text{C}$
3	<i>w</i>	pyridine	345.00
19	<i>r</i>	pyridine	345.00
4	<i>w</i>	acetic acid	321.30
5	<i>r</i>	acetic acid	321.30

\*) Because of technical difficulties the method of comparative measurements could not be applied [5].

According to Pawlewski's rule, the change in temperature  $T_m$ , occasioned by the change in the composition of the mixtures, should be re-

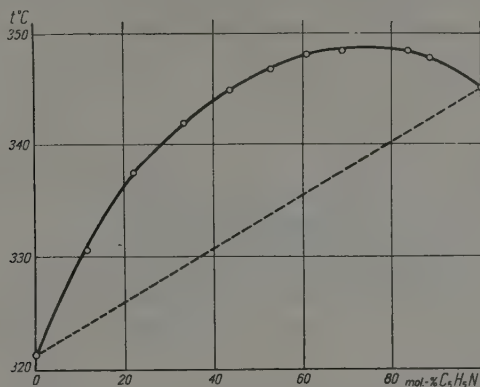


Fig. 1. Critical temperatures of mixtures of acetic acid and pyridine. The dotted line corresponds, to a system showing no deviations from Pawlewski's rule

#### Mixtures of acetic acid and pyridine:

Tube No.	Degree of filling	Composition of mixtures in mole per cent		$T_m$ °C.	$(T_i - T_m)$
		$C_5H_5N$	$CH_3COOH$		
10	w	11.7	88.3	330.60	— 6.8
9	w	21.8	78.2	337.50	— 10.8
8	w	32.9	67.1	341.85	— 12.6
11	k	43.5	56.5	344.85	— 13.1
7	r	52.7	47.3	346.70	— 12.9
18	r	60.7	39.3	348.10	— 12.1
6	k	68.7	31.3	348.35	— 10.8
17	r	83.6	16.4	348.35	— 7.2
16	w	88.4	11.6	347.70	— 5.4

presented by a straight line. Thus  $(T_i - T_m)$  — values determined graphically — represent deviations from this rule. The largest deviation was found in the case of a mixture in which the mole ratio equalled, approximately, 1:1.

It was found that the mixture containing  $75 \pm 1$  mole per cent of pyridine had the highest critical temperature  $T_m = 348.5 \pm 0.05^\circ$ , which is  $3.5^\circ$  higher than the critical temperature of pure pyridine.



### Summary

The system of acetic acid-pyridine forms a negative azeotrope in the critical state, composed of  $75 \pm 1$  mole per cent of pyridine. The temperatures  $T_m$  of the disappearance of the meniscus of pure pyridine, pure acetic acid and of the azeotrope are  $345.0^\circ$ ,  $321.3^\circ$  and  $348.5^\circ$  respectively.

Department of Physical Chemistry, University of Warsaw

### REFERENCES

- [1] Świętosławski W., *Roczniki Chem.* **26** (1952), 632.
- [2] Kuenen J. P., *Z. Physik. Chem.* **37** (1901), 483.
- [3] Dewar J., *Proc. Royal Soc. (London)*, **30** (1880), 538.
- [4] Horsley L. H., *Anal. Chem.* **19** (1947), 508.
- [5] Świętosławski W., Zięborakowa, in press.
- [5] Świętosławski W., Pieszczek S., *Bull. Intern. Acad. Sc. Polon.* **A-1937**, 72.

## Electric Phenomena Accompanying Flotation

by

B. KAMIŃSKI and A. POMIANOWSKI

*Communicated by B. KAMIŃSKI at the meeting of November 16, 1953*

In several earlier papers it was shown by one of the above authors, that the substances used in the flotation process influence the electric potential of conducting minerals [1]—[11]. Thus xanthates depress the potential of an electrode made from galena. There are marked changes in the potential and these appear immediately after collectors are added to a pure solution into which an electrode prepared from a conducting mineral has been submersed. The xanthates are adsorbed on the mineral and thus suitable conditions are procured for the flotation process. The simultaneous use of both frothers and a gas phase is necessary to ensure an efficient process. Earlier experiments confirmed the theory, by means of which it is possible to predict that frothers will not change the potential of the electrode but that they will change markedly the electric potential on the free surface of the solution (air) [12]. A mixture of collectors and frothers was used to supplement each other during flotation.

The purpose of these experiments was to ascertain whether the potential changes detected in pure solution composed of distilled water and an electrode (mineral) would also appear in the more complicated conditions of actual flotation, where, instead of one single mineral electrode, a dense and mobile suspension of the ore is applied. The surface of a single particle of mineral serving as an electrode is very small in comparison with the very great surface of the crushed ore, and a new greatly extended surface of air (solution) appears during actual flotation, where great quantities of air (oxygen) are introduced into the pulp and ordinary water is used. The oxidising atmosphere and casual catalysts such as e. g. iron oxides, present in the ore, may also be of some importance. If electrical phenomena were to appear in these complicated conditions, the investigation of the process of flotation by means of very convenient electrical methods would be possible.

In order, therefore, to obtain some information on this question a celluloid experimental flotation apparatus was constructed. A schematic picture of the flotation cell is given in Fig. 1. At the bottom, air was inflated into the suspension which had been mixed thoroughly by the propeller *M*. In order to enhance the efficiency of the cell a celluloid grate *A* was constructed in the middle so that the crushed particles of the mineral could be dressed

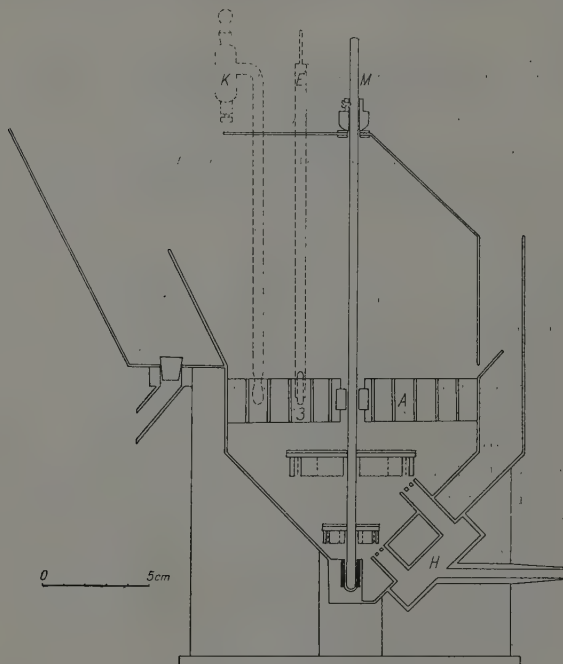


Fig. 1

easily by air bubbles and floated to the surface without interfering with the destructive whirlpools in the lower parts of the cell. A selected particle of galena, serving as an electrode, was sealed tightly into the end of a glass tube and put into the suspension. In that way it was possible to check the potential of the mineral particles by comparing their potential with that of a saturated calomel electrode *K*. Both electrodes were connected with a quadrant electrometer (Lindemann electrometer, Cambridge Instrument Co. having a short period and small capacity, and the potential of the mineral electrode was measured without interruption. The number of revolutions of the propeller *M* (Fig. 1) could be changed conveniently (700 to 1400 rev. per minute). The cross section of the cell was circular to avoid dead spaces and irregular whirlpools. If the volume of the cell is rather large, rectangular

cross sections do not prevent efficient mixing — if, however, small experimental cells are operated, irregular whirlpools become troublesome and a circular cross section is advisable. The electrode made from galena had the shape of a short rod (Z) one centimetre or more in length and was sealed at one end into a glass tube with a cross section of c. 7 mm.<sup>2</sup>. Some mercury drops put into the glass tube ensured good contact with an electric wire and with the electrometer. After adjusting the electrometer so as to secure suitable sensitivity and stabilising the acidity with sulphuric acid or sodium carbonate, the propeller and compressed air circulation were put into operation and a mixture of crushed galena and sand was poured into the cell. The average size of each crushed galena and sand particle was c. 0.1 mm. in diameter. Artificial mixtures e.g. of 3% galena and 97% sand, were applied. Then the flotation agents were added to the pulp. They consisted of an emulsion of 1 g. potassium ethyl xanthate and 1 g. of terpeneol in 250 c. c. distilled water. The volume of the suspension was 900 c. c. of ordinary water. A mass of 90 g. of the artificial ore was put into the water. This time the artificial ore consisted of 90% sand and 10% galena (Fig. 2). A volume of 20 c. c. emulsion (xanthate with terpeneol in water) was applied as a flotation agent. The ordinate in Fig. 2 represents the potential of the electrode against the time as abscissa. Arrows indicate the moments of pouring the crushed ore into the cell and similarly the moments of putting the emulsion into the suspension.

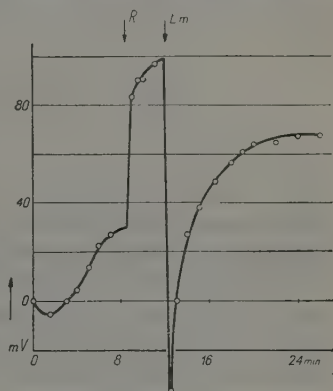


Fig. 2

The ordinate in Fig. 2 represents the potential of the electrode against the time as abscissa. Arrows indicate the moments of pouring the crushed ore into the cell and similarly the moments of putting the emulsion into the suspension.

The potential of the electrode (PbS) increased with time under the action of air; when the ore was put into the cell a further increase took place. After 12 minutes had elapsed the emulsion was poured into the cell. An instantaneous decrease in the potential (c. 100 mV) was observed. At the same time galena appeared in the froth and was efficiently floated in the short space of several minutes. The potential slowly rose again when the mineral was thrown out of the cell by the froth. The pH index of the suspension was 3.

The next experiment was carried out under changed conditions. The portion of ore was increased to 200 g. (containing 3% lead sulphide). The acidity was limited to pH 7.5–8.0. Only 10 c. c. emulsion were applied. As may be seen in Fig. 3, the potential of the electrode is more stable in an alkaline solution. The addition of the emulsion was signalized by a sudden change in the potential during which the flotation of galena took place effectively. Ferric ions cannot be present in alkaline solutions and that is the reason why the potential of the electrode is more stable before the

emulsion is added to the pulp. The potential of the electrode increases during the flotation process and this fact indicates a decrease in the xanthate concentration, or a decomposition of the instable chemical compound. If we compare Fig. 2 with Fig. 3 we may observe some similar characteristic points and also some different ones. The moment of flotation is accompanied by a sudden potential decrease, depending on the acidity of the pulp. The

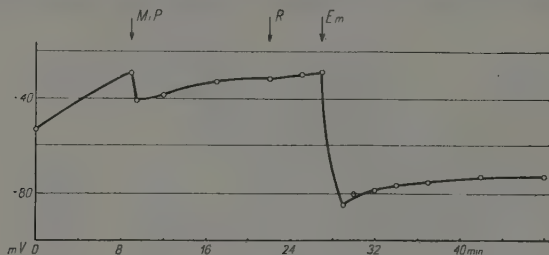


Fig. 3

more alkaline the pulp becomes, the smaller is the potential change, and the general potential of the electrode shifts to more negative values. Since the change in potential is negative when the solution becomes alkaline, it may be assumed that the galena electrode is sensitive to hydrogen and hydroxyl ions. This corroborates some earlier observations made in the papers cited below. The influence of hydrogen ions during actual flotation is a problem which should be elucidated more fully.

Laboratory of Physical Chemistry and Electrochemistry, Jagellonian University.  
Cracow

#### REFERENCES

- [1] Kamiński B., *Z. physik. Chem. (A)* **138** (1928), 345.
- [2] — (A) **145** (1929), 48.
- [3] — (A) **147** (1930), 288.
- [4] — *Przemysł Chemiczny* **15** (1931), 201.
- [5] — *Z. Physik. Chemie (A)* **158** (1932), 441.
- [6] — *Congrès International d'Électricité*, Paris 1932, 7e Section, Comn. No. O—C.
- [7] — *Nature*, **129** (1932), 59.
- [8] Kamiński B. and Karczewski K., *Przemysł Chemiczny*, **17** (1933), 33.
- [9] — *Roczniki Chemii*, **14** 383, 394 (1934), 373.
- [10] Kamiński B. and Benis L., *ibidem*, **16** (1936), 81.
- [11] The same *ibidem*, **17** (1937), 89.
- [12] Kamiński B., *Roczniki Chemii* **17** (1937), 497—528.



## The Influence of Hydrogen Ions on the Potential of a Mineral Electrode during the Process of Flotation

by

B. KAMIENSKI and A. POMIANOWSKI

*Communicated by B. KAMIENSKI at the meeting of November 16, 1953*

In earlier papers quoted by the authors in their last publication attention was called to the influence exerted by a hydrogen ion concentration on the potential of minerals such as galena, pyrite, chalcopyrite, pure graphite, etc. The less able the chemicals are to attack the electrode, the more regular is the action of the hydrogen ions on the electrode. The surface of each mineral is, however, easily polarised electrochemically if, when measuring the potentials, we adopt the most widely practised methods. In order to prevent changes taking place in the surface through polarization, a quadrant electrometer of small capacity, such as e. g. Lindemann's electrometer, was used. When pure chemicals are used and neither crushed ore nor air is inflated into the solution the change in the potential of the electrode reminds one to some extent of the behaviour of the potential of a hydrogen electrode when immersed in a pure solution at different ion concentrations, as was described in several earlier papers. There are, however, some quantitative differences between the behaviour of conductors, such as e. g. platinised hydrogen electrodes, and semiconductors such as e. g. conducting sulphides or graphite. In earlier papers it was assumed that the potential of unattackable electrode depended on the adsorption of the smallest ions, i. e. hydrogen ions and hydroxyl ions, on account of the fact that a stream of electrons accompanies the adsorption of ions in the conductor, in consequence of which the potential of the electrode changes.

The separation by flotation of different minerals (semiconductors) is subject to certain limitations imposed by the various hydrogen ion concentrations of the pulp. It was interesting to study not only the influence of hydrogen ions on the efficiency of flotation, a fact which is fairly well known in most practical cases, but also their influence on the potential which is regarded by us as an indicator of the process of flotation. In prac-

tical flotation different factors are met with which do not appear when pure solvents are used. These factors include the action of the air, the oxidation of the mineral under the influence of oxygen and catalytic agents such as iron and manganese salts, and finally the presence of oxides which do not appear in pure solutions.

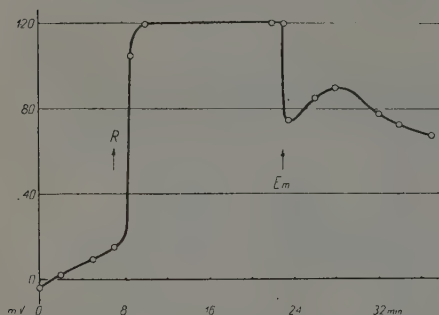


Fig. 1

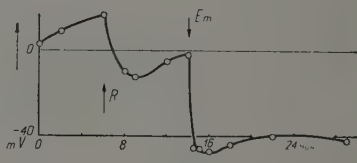


Fig. 2

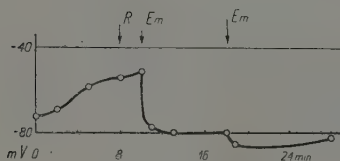


Fig. 3

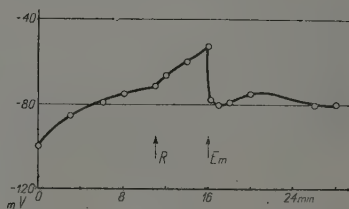


Fig. 4

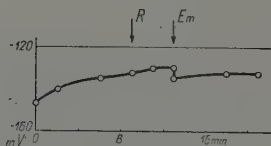


Fig. 5

A flotation apparatus similar to the one described in a recent paper was used to measure the potentials of electrodes (PbS) during the flotation process. Experiments were carried out using five different hydrogen ion concentrations, beginning with pH 2.1 to 2.2 in the first experiment (Fig. 1), pH 3.8 to 4.4 in the next experiment (Fig. 2), pH 7.5 to 8 in the third experiment (Fig. 3), pH 8.5 to 9 in the fourth experiment (Fig. 4) and lastly pH 10 to 10.4 in the last experiment (Fig. 5). The potential of a galena

electrode was measured against a saturated calomel electrode, both electrodes being submersed into the pulp during flotation. The ordinate represents the potential of the mineral electrode, the abscissa the time (Fig. 1, 2, 3 4 and 5). Arrows denote the moments of pouring the crushed ore into the flotation cell and also the moment of adding the flotation agents (an emulsion of 1 g. potassium ethyl xanthate and 1 g. terpeneol in 250 g. water). The measurements were taken during the flotation process. 850 c.c. of water were used and the concentration of hydrogen ions was regulated by suitable additions of sulphuric acid or sodium carbonate. Ordinary water is quite an efficient buffer solution, especially in the presence of crushed ore. A mass of ore, weighing 170 to 180 g. and containing 10% galena and 90% sand sized to a diameter of circa 0.1 mm., was put into the cell. A volume of 7 c.c. of emulsion was added. Comparing the shift of the potential with the varying hydrogen ion concentration, we see that the weaker the hydrogen ion concentration, the more negative the potential. At the same time the smaller the amount of acidity, the weaker is the action of xanthate on the potential. This is obvious when we consider the drop in the potential at the moment of adding the emulsion. Immediately upon the addition of the flotation agents (emulsion), froth appeared, together with lead sulphide free from sand. It should be noted that when the pulp is alkaline (Fig. 5), the drop in the potential is small at the moment of adding xanthate. At the same time the recovery of lead sulphide is poor. In general the most significant point of the diagram is the moment of adding the emulsion and the accompanying drop in the potential. It was of interest to determine by the electrical method the change in the concentration of the adsorbed xanthate. Potassium xanthate seems to be unstable in acid solutions, but more stable in an alkaline medium in which it is ionised. In order to ascertain whether this is really so, a fresh quantity of xanthate was poured into the solution after the process of flotation had come to an end. If no trace of the xanthate had been left in the solution, in other words, if the whole quantity had been thrown out with the froth, then the potential of the electrode should have changed, when a fresh amount was added. The third experiment (Fig. 3) represents such a case. A quantity of emulsion (7 c.c.) was added after the flotation process had ended. As may be seen from Fig. 3 this addition caused only a slight change in the potential and this result shows that an appreciable quantity of the xanthate was left in the solution. In acid solutions, on the other hand, the deflection of the electrometer needle is less stable (Fig. 1) whenever the reaction of the pulp is acid, and so it may be assumed that the stability of xanthate is less in these media.

As may be seen in Fig. 1 to 5, the change in the potential varies, with different conditions, and so a new series of experiments was made, in which the concentrations of emulsion, the amount of ore, and the hydrogen ion concentration were all changed. The upper curve in Fig. 6 represents the

drop in the potential of the galena electrode when 80 to 95 g. crushed ore (a synthetic mixture of sand and galena) were floated in 900 c.c. water and 20 c.c. of the emulsion were added during every flotation process. The

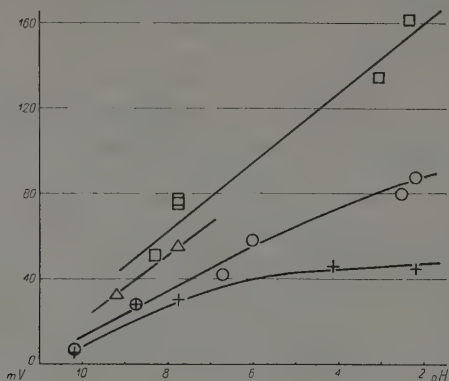


Fig. 6

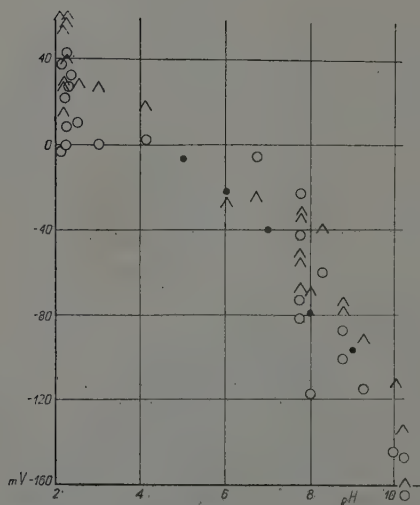


Fig. 7

five points on the curve represent five flotations on the same quantity of ore at different pH. In the next series, the lower curve represents two experiments in which 200 g. synthetic ore (3%) were floated with the aid of 700 c.c. of water and 10 c.c. of the emulsion. The curve still lower represents drops in the potential in 5 separate experiments, in which no ore

was added, but in which air was inflated and 7 c.c. of emulsion were used in 900 c.c. of water. The last series (nearest to the abscissa) represents the varying drops in the potential which were observed in the five experiments already described (see Figs. 1—5). A mass of ore 170 to 180 g., 850 c.c. of water, and 7 c.c. of emulsion were used. We see from Fig. 6 that the smaller the amount of ore and the greater the quantity of emulsion, the greater is the drop in the potential at the moment of pouring the emulsion, into the solution, and similarly the greater the acidity the greater is the drop in the potential. If we compare the potentials of the electrode as a function of the hydrogen ions at the moment of submerging the electrode and after the lapse of 7 minutes, we can see (Fig. 7) that the potential increases with the growing strength of the hydrogen ion concentration. In Fig. 7 all the available experimental measurements are to be found. The pH of the solution is marked on the abscissa and the potentials of the electrode (against a saturated calomel electrode) are represented on the ordinate. Points and circles represent the potential of the electrode at the moment of submerging the latter into the pulp, rooflets represent the potential after 7 minutes. The measurements are a synthesis of all those made during the flotation experiments and quoted in these papers. In diagram 7 the measurements of the potentials lie within a defined area and so it may be assumed that hydrogen ions and hydroxyl ions are adsorbed on a semiconductor electrode whenever it is able to resist chemical action.

Laboratory of Physical Chemistry and Electrochemistry, Jagellonian University, Cracow





## Electrical Action of a Flotation Depressing Substance

by

B. KAMIŃSKI and A. POMIANOWSKI

*Communicated by B. KAMIŃSKI at the meeting of November 16, 1953*

Some minerals, e. g. mineral sulphides (galena), swim easily when subjected to the flotation process; consequently, it is sometimes necessary to suppress this tendency of theirs to swim with the froth. This we can do by using a process of selective flotation, whereby several minerals are separated one after another. One of the most active depressors in the case of lead sulphide is potassium bichromate. Galena resists many chemical reagents and it is a semiconductor which changes its potential when immersed into an acid or alkaline solution. The mineral preserves its conductivity on the surface. In view of these facts, we are able to predict the sensitivity of galena to redox systems. On the other hand, strong oxidising agents may oxidise the surface of the mineral and change the conditions of conductivity on the surface. The question then arises as to whether a lead sulphide electrode is sensitive to the action of bichromate. Taking into account the high positive valency of chromium, we can expect it to influence the unassailable electrode and change its potential. Xanthates depress the potential of the electrode and flotation begins when the potential is low.

In order to investigate whether potassium bichromate changes the potential of the electrode, we used a flotation cell containing a lead sulphide electrode and a calomel electrode such as are described in preceding papers. A volume of water (810 c.c. was acidified with a volume of 90 c.c. 0.1 N sulphuric acid, and 180 g. synthetic ore, 10% galena, 90% sand) were poured into the acid solution. In Fig. 1 this moment is marked by an arrow. The potential of the lead sulphide electrode rises when air is inflated into the pulp. This can be observed in Fig. 1. But, when a solution of 1 c.c. bichromate (containing 25 g. potassium bichromate in 250 c.c. water) is added to the pulp there is a sudden and much greater increase of the potential. A sharp maximum appears in the potential followed almost immediately by a rapid decrease. In Fig. 1 three arrows indicate the fact that three separate quantities of potassium

bichromate were added, twice a quantity of 1 c.c. and the third time a greater quantity of 2 c.c. The potential rose each time, but the increase each time was smaller and more stable. The sudden changes in the potential are due to oxidation of the electrode (rise), and to the reduction of bichromate caused by the very great surface of the mineral (decrease). The surface of the lead sulphide changed in the course of the

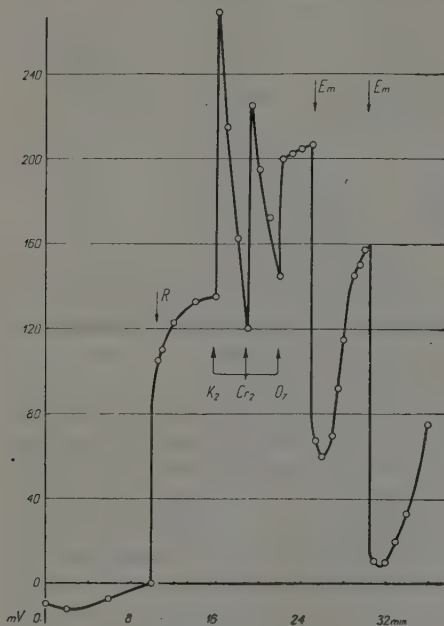


Fig. 1.

the electrode. It is much better to use the sharp edges of hard dielectrics (glass).

When reviewing the results, it should be noted that bichromate raises the potential of the galena electrode, thus acting as a depressor, whereas, xanthates lower the potential, thus acting as a flotation agent.

Laboratory of Physical Chemistry and Electrochemistry, Jagellonian University, Cracow

prolonged action of bichromate, but we expected that xanthate would change the potential of the electrode. When 7 c.c. emulsion (1 g. xanthate, 1 g. terpeneol in 250 c.c. water) were poured into the cell, a sharp drop in the potential was observed but it rose rapidly again (see Fig. 1). The action of the emulsion was of short duration and no flotation took place, notwithstanding thorough mixing, air blast and the addition of flotation agents. The electrode used during the experiments was poisoned and did not react normally in further experiments. Even mechanical cleansing with sharp edges of broken glass was not effective. Metallic edges should be avoided when scratching off the surface of the electrode as they influence the potential of

## Sur l'âge de formation des dômes salifères sur l'anticlinorium de Couyavie

par

J. SAMSONOWICZ

*Présenté à la séance du 16 Novembre 1953*

Les dômes salifères de l'anticlinorium de Couyavie s'élèvent à partir de gîtes primaires qui reposent à des profondeurs très considérables. Étant soumis à une énorme pression des couches susjacentes ainsi qu'à des modifications chimiques dépendant du métamorphisme thermal, ils semblent avoir profiter lors de leur ascension de puissantes failles qui coupent les sédiments mésozoïques dans deux directions, transversalement et parallèlement à la direction de l'anticlinorium de Couyavie, et qui se croisent au voisinage de son bord sud-ouest.

L'anticlinorium de Couyavie (la „Tempelburger Achse” des géologues allemands) s'étend le long de la zone axiale de la vaste cuvette du Zechstein, où les dépôts mésozoïques remplissant cette cuvette atteignent leurs plus grandes épaisseurs: l'épaisseur des sédiments du Malm dépasse 520 m., du Dogger — 560 m., du Lias — 750 m. et celle du trias — 1500 m. La cuvette du Zechstein se présente donc comme une fosse, qui, durant la sédimentation, tant continentale (périodes du Grès Bigarré, du Keuper et du Lias), que marine (périodes du Muschelkalk, du Dogger et du Malm) était soumise à un enfoncement permanent et avait donc le caractère d'un géosynclinal.

L'épaisseur totale des dépôts mésozoïques de la zone de l'anticlinorium de Couyavie dépasse de beaucoup 3000 m. Ce n'est donc qu'à cette profondeur ou au delà que l'on peut s'attendre à atteindre les gîtes salifères du Zechstein supérieur *in situ*.

Les dômes salifères s'élèvent donc d'une profondeur dépassant 3000 m., ce qui est conforme aux résultats des forages exécutés à l'anticlinorium de Couyavie. L'un de ces forages n'a pas atteint la base du dôme à une profondeur au-dessus de 2400 m., un autre n'a pas percé le dôme à une profondeur de 3026 m. Les profondeurs des couches salifères non affectées tectoniquement doivent donc être encore plus élevées. On a constaté au NO de

l'Allemagne que les profondeurs d'où s'élèvent les dômes sont de 3800 m. au moins, et pour les parages de Hambourg — de 5000 m. [1]. — Dans la partie orientale du Texas les dômes salifères qui émergent du Crétacé inférieur et percent le Crétacé inférieur et supérieur ainsi que le Paléogène et qui ont leur chapeau de gypse dans le Miocène (p. ex. à Humble Dome), n'ont pas été traversés par les forages à 4000 m. de profondeur. Les recherches sismiques ont démontré que ces dômes peuvent provenir d'une profondeur de 25000 – 30000 pieds soit 7500—9000 m. [2].

D'après Riedel [3] on n'a réussi nulle part au NO de l'Allemagne à constater la connexion des dômes de sel avec leurs couches primaires reposant à de grandes profondeurs. Riedel, se basant sur les données concernant les mouvements ascendants des dômes salifères du NO de l'Allemagne, affirme que certains de ces dômes s'élevaient d'une façon continue et uniforme pendant le Crétacé, le Tertiaire et le Pléistocène, et qu'ils ont encore de nos jours une tendance à l'ascension; d'autres ne s'élevaient que pendant les phases orogéniques, mais se trouvaient en repos durant les périodes de calme orogénique. Lors des mouvements ascendants certains dômes atteignaient la surface, où ils furent dénudés et recouverts par les sédiments de transgression successive, puis ils revivaient et reprenaient leur ascension. D'autres n'atteignaient pas la surface mais ils causaient l'élévation des dépôts du toit. Les dénudations de ces derniers causaient les discordances ainsi que des lacunes dans leurs séries.

B. Świdorski [4] supposait l'existence des mouvements ascendants des dômes salifères sur l'anticlinorium de Couyavie durant le Pléistocène. P. Dorn [1] est d'avis que l'ascension des masses de sel se trouvait en rapport avec les phases orogéniques saxonniennes; néo-cimmérienne, subhercynienne et tertiaire, et même en partie avec les mouvements au Quaternaire. Il affirme, que les formes actuelles des massifs salifères se produisirent pendant le Néogène. Il attribue aussi la formation de l'anticlinorium de Couyavie à l'orogénie saxonnienne, et notamment à sa phase paléogène ([1], p. 53).

Les faits observés lors de certains forages exécutés sur l'anticlinorium de Couyavie complètent et modifient dans une certaine mesure les opinions émises sur l'âge des dômes salifères et sur l'âge de la formation de l'anticlinorium lui même.

Un forage aux environs de Kłodawa a atteint sous les dépôts du Miocène et au-dessus d'un chapeau d'anhydrite du dôme salifère une série de 43 m. d'épaisseur d'argiles de couleur rose ou brique, puis blanches, gris et noirs vers le bas et enfin verdâtres dans leur partie inférieure. On observe quelques minces intercalations de grès à grains fins. Les argiles sont fortement triturées. Elles contiennent de nombreux fragments d'anhydrite, subanguleux et menus, n'atteignant que rarement 15 cm. de diamètre.

Dans un autre forage, exécuté sur le versant nord du dôme salifère, on traversa, sous une épaisse série de grès du Lias inférieur, une série de



sédiments keupériens de 230 m. d'épaisseur. Elle consiste d'argiles de couleur gris, brique et vert, contenant de nombreux fragments subanguleux d'anhydrite. Dans la partie inférieure de cette série, directement sur le chapeau d'anhydrite, recouvrant le dôme salifère du Zechstein, se trouve une couche de 4.9 m. d'épaisseur de pseudo-oolithes (ooïdes, Rogenstein), très caractéristiques pour le Keuper des autres régions de la Pologne, comme par exemple pour le versant NE du massif de Ste. Croix. Cette roche contient aussi de nombreux fragments anguleux d'anhydrite, ce qui lui confère un caractère de brèche.

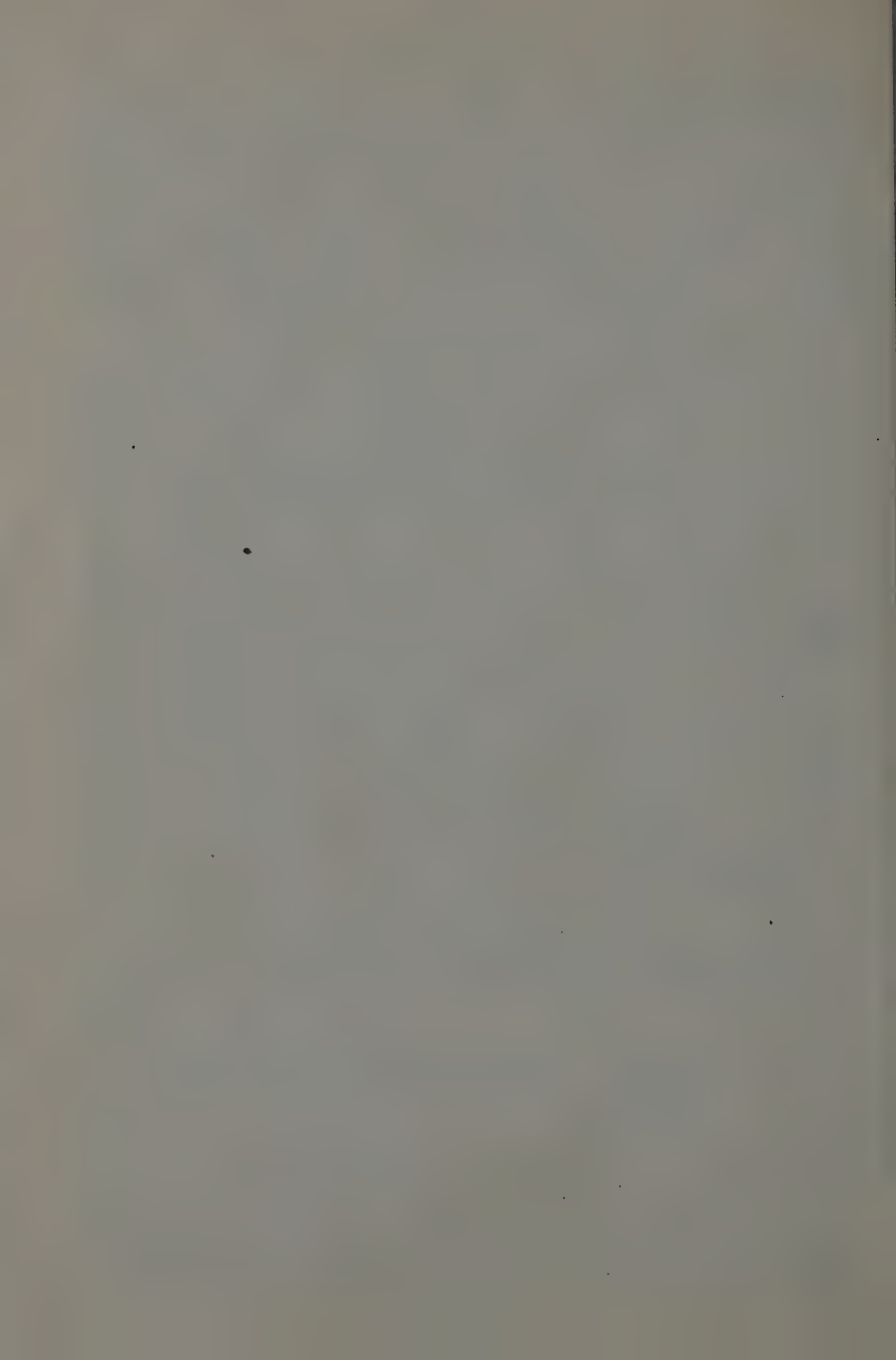
Les fragments d'anhydrite dans les sédiments keupériens proviennent certainement du chapeau d'anhydrite au-dessus du dôme salifère. Il est permis d'en conclure que durant la sédimentation du Keuper *le dôme salifère avec son chapeau d'anhydrite existait déjà et était sujet à une dénudation* au fond du bassin de sédimentation. L'âge du dôme salifère est donc pré-keupérien et le dôme fut élevé dans une phase jusqu'à présent inconnue d'orogénie éo-cimmérienne. Je propose de donner à cette phase le nom de phase Couyavienne.

Il semble, d'après les faits cités, que l'émersion de l'anticlinorium couyavien a commencé avant le Keuper. Pendant la période jurassique les mouvements de soulèvement ont été remplacés par des mouvements contraires — de subsidence, ce qui a rendu possible une nouvelle sédimentation et une accumulation de très épais dépôts: continentaux du Lias et marins du Dogger et du Malm. Dans le temps post-jurassique les mouvements ascendants du dôme salifère se sont renouvelés et semblent s'être continués jusqu'au Pléistocène. Peut-être se manifestent-ils même jusqu'à présent.

Laboratoire de Géologie Stratigraphique de l'Université de Varsovie

#### OUVRAGES CITÉS

- [1] Dorn P., *Geologie von Mitteleuropa*, Stuttgart 1951.
- [2] Nettleton L. L., Bull. Geol. Soc. of America, **63**, No. 12 (1952).
- [3] Riedel L., Jb. d. Reichsamt f. Bodenf., (1942), **63**, Berlin 1944.
- [4] Świdorski B., Kosmos **46** (1922).



## Heavy Minerals as Correlation Indices of Cracow Soils

by

J. TOKARSKI and J. BRZozowski

*Communicated by J. TOKARSKI at the meeting of March 16, 1953*

In the Soil Science Institute of the Jagellonian University a fundamental reform of some investigation methods of soil profiles was introduced in recent years. As every soil, deprived of its external and inconstant components — above all of air and water — consists, as regards its volume, mainly of mineral and organic parts, it was decided to pay attention to the quality and quantity of the first predominant part of soil elements. All soil properties, including its fertility, doubtless depend on the physical, chemical and morphological characters of those mineral soil elements.

The important problem of soil classification, which ought to be based on natural principles, can be rationally solved among others on the basis of a thorough knowledge of mineral soil composition. Until now this point of view was not taken into account in modern, and still young soil-science. The cause lies in the analytical difficulties of getting acquainted with the soil, which as a rule required very numerous and special analyses. For reasons unknown soil scientists did not profit by the experiences of a kindred science, petrography, which disposes of excellent methods for determining various kinds of minerals, even by X-rays.

We find in every soil the following mineral components: quartz sand, carbonates, clay components, alongside organic parts designated as humus. The quantitative proportions of these components can vary considerably, even in a small area, both in a horizontal and vertical direction. A so-called soil profile cannot be considered as a separate soil unit but as a small part of any unit constituted of a large quantity of varying profiles.

A genetic soil classification has to take into account historical evolutionary circumstances. This problem can be solved by a comparison of the evolutionary facts of the soils of a given area, determined by means of suitable analysis. In other words, only exact analytical data of profiles of

all levels including the subsoil can furnish the material needed for a suitable comparison.

The present work is the first attempt to compare soils on the basis of their contents of so-called "heavy minerals" as components of a rock substratum. We give this name to the mineral components present in all kinds of soil regoliths in very small quantities and often in characteristic complexes.

They differ from common rock constituents by their high specific weight (over 3), insolubility in acids, high light refraction coefficients and a considerable hardness. Their dimensions are usually small and their crystalline forms are sometimes perfectly preserved. They were formed as accessory components in magma rocks and came out undestroyed by a process of mechanical and chemical decomposition of the latter. They were then washed off from the decomposed surfaces of magma rocks and later came to sedimentation basins, where they finally formed the mineral parts of sedimentary rocks.

Various types of magma-rocks contain particular complexes of heavy minerals. Since sedimentary rocks arise primarily from decomposed magma-rocks, it is obvious, that on their various levels corresponding complexes of heavy minerals can be found. This fact was used in micro-geological investigations for correlation or paleo-geographical purposes.

Soils are formed chiefly from so-called regolithe, or rocky fragments which always appear on the boundaries between the rocky crust of the earth and the atmosphere. Regolithe, according to its sedimentary or magmatic origin, can contain various characteristic complexes of heavy minerals. These can, therefore, indicate the stratigraphic position of the regolithe. In a soil formed under the influence of climatic and especially biologic agents, the heavy minerals remain for the most part unchanged and, what is of particular importance, in unchanged complexes. We could, therefore, establish by analysing these complexes, the origin of the regolithe in the soil and further the evolution of soil profiles. An attempt to correlate soils by comparing their complexes of heavy minerals was undertaken in Poland for the first time in the Institute of Soil Science of the Jagellonian University in Cracow. The soils of the Cracow district were used as an experimental field for this purpose, since their arable part was thoroughly studied in the last years and they were embraced in a natural classification scheme. The following types belong to them: loose sands, light and heavy sands, light and heavy loams and diluvial loess. For the sake of comparison a similar analysis was made of Vistula sand now used to filter water in Cracow. After a suitable preparation of mean specimens of those soils, their heavy minerals were separated with the aid of bromoform, finally enclosed in microscopic separations and submitted to qualitative and quantitative analyses. The latter consisted in a calculation of the percentages of various mineral species for a given kind of soil. The results of this analysis are

shown on the enclosed table. Percentage data were obtained from the following quantities of grains, counted in microscopic preparations:

Vistula sand — 2,110,	loose sand — 9,055,
light sand — 926,	heavy sand — 2,841,
light loam — 939,	heavy loam — 1,244.

The preparations were made from specimens of at least 50 g., up to 200 g. each. The results of calculating on such a considerable number of grains guaranteed the exactitude of measurements. To obtain comparable pictures of all kinds of specimens, they were represented geometrically. In the enclosed concentration triangle three characteristic minerals were placed on the corners, i. e. garnet, tourmaline and zircon. The quantities of these minerals, the sum of which was calculated as 100%, made it possible to represent every specimen of the investigated material as a point on the surface of the triangle. Three parameters of given points illustrated the percentages of contents of the three minerals placed on the corners of the triangle mentioned. Beneath the triangle, and in accordance with the course of the garnet line, a geometrical gauge was placed, on which the position of two further groups of minerals characterizing the investigated object by means of microscopic analysis was stated with the help of ordinates. The groups were:

1. the staurolite group, comprising the sum of the following minerals: staurolite + sillimanite + andalusite + kyanite + corundum;
2. the rutile group comprising the sum of: rutile + brookite + titanite + either amphibole (a) or biotite (b).

Thus each investigated material was characterised by three points, positions of which, in respect to the three projection bases exactly illustrated the differences of contents of the characteristic complexes obtained by microscopic investigations.

The investigations gave the following results:

1. Heavy minerals could be isolated in notable quantities from every kind of soil. Among them there were found: garnet, zircon, tourmaline, staurolite, sillimanite, andalusite, kyanite, corundum, rutile, brookite, titanite and amphibole.

2. The quantitative proportions of these minerals were different for each kind of soil. On this basis two fundamental groups of soils could be distinguished: the first group comprised loose, light and heavy sands, as well as light loams; the second group comprised loess and heavy loams. The first group was characterized by similar percentages of garnet and zircon, and a nearly similar content of the staurolite and rutile groups. The second group was characterized by higher quantities of zircon, lower quantities of garnet, similar quantities of the staurolite group, and higher content of the rutile group.



TABLE  
of heavy minerals (in quantity percentages)

Specimen	Vistula sand	Loose sand	Light sand	Heavy sand	Light loam	Heavy loam	Loess from Mogiła	Krosno		layers
								Żółków	Besko	
Garnet	33	45	40	41	41	26	16	85		65
Zircon	13	23	17	22	18	27	27	3.5		2
Tourmaline	12	6	21	9	11	13	14	4		4
Staurolite	21	14	6	14	15	9	21	3		3
Sillimanite	tr.	tr.	tr.	tr.	—	2	2	tr.		1
Andalusite	10	6	2	5	4	tr.	1	tr.		—
Kyanite	tr.	tr.	tr.	tr.	1	1	—	tr.		tr.
Corundum	tr.	tr.	1	tr.	1	1	—	—		1
Rutile	8	6	12	8	6	16	9	3.5		3
Brookite	1	tr.	1	1	1	2	—	—		tr.
Titanite	1	tr.	—	tr.	—	2	—	—		tr.
Amphibole	1	tr.	—	—	2	1	10	tr.		—
Biotite	—	—	—	—	—	—	tr.	1		21
Calculated-number of grains	2110	9055	926	3841	953	1294	—	—		34500



The second group is also characterized by the appearance of a higher quantity of amphibole.

3. The first group is similar in its proportions to the sands conveyed at present by the river Vistula. The proportions appearing in the second group approach those of diluvial loess.

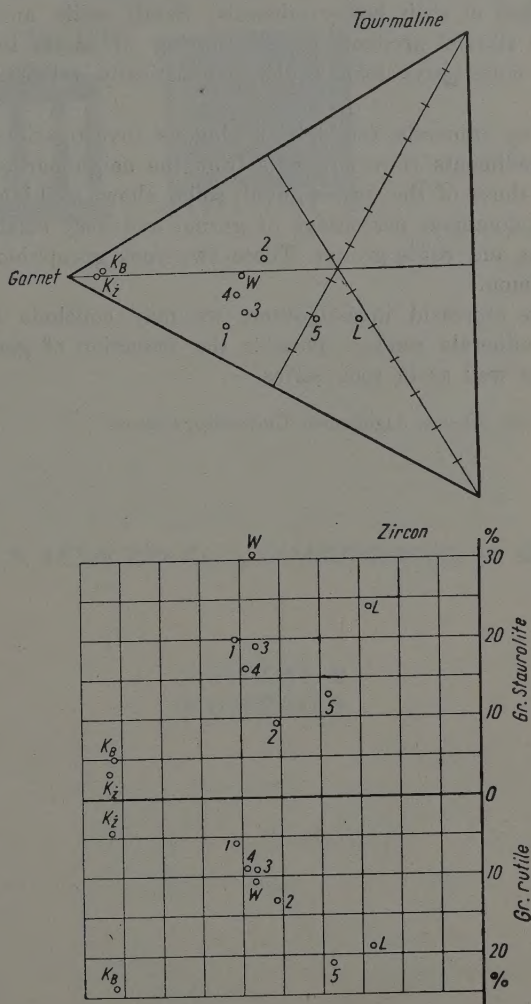


Fig. 1. Concentration triangle

4. A series from loose sands to light loams, differentiated by increasing quantities of tourmaline, appears in the first group. The increase observed

in the percentage of this mineral seems to be a function of the reduced grain size of the soil. The correlation between this group and contemporary Vistula sand is an index of its genesis. The second group seems to be a derivative of loess.

5. The geological appearance of the investigated soils is connected with the analytical data of their heavy minerals. Sandy soils and light loams were formed as alluvial products by the sorting of sands in part of the Vistula valley, while heavy loam could be genetically related with eroded loess.

6. The heavy minerals found by analogous investigations in a series of Carpathian sediments (Krosno-layers from the neighbourhood of Besko) compared with those of the investigated soils, show striking differences. They contain a dominant percentage of garnet and very small percentages of the staurolite and rutile groups. These two rock groups have, therefore, nothing in common.

7. From the aforesaid investigations we may conclude that the analysis of heavy minerals renders possible the deduction of genetic correlations in soils, as well as in rock series.

Institute of Soil Science, Jagellonian University, Cracow